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INORGANIC CHEMISTRY

BY

FRANK AUSTIN GOOCH
PROFESSOR OF CHEMISTRY IN YALE UNIVERSITY

AND

CLAUDE FREDERIC WALKER
TEACHER OF CHEMISTRY IN THE HIGH SCHOOL OF COMMERCE
OF NEW YORK CITY

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PREFACE

In this new presentation of a plan of study which in the main has been put to long test in school and college work, it has been our aim to introduce the student to chemistry by consideration of the simplest and fewest things. We have tried to put the experimental phenomena in such relation that the inferences may not be missed.

Part I takes up the consecutive experimental development of the principles upon which systematic chemistry rests. The consideration of identity of substances, chemical change, the chemical elements, the laws of combination, and chemical equivalents, naturally comes first. Electrical phenomena and ions, — the ions of Faraday, — the constitution of acids, bases, and salts from this ionic point of view, the conditions of action and equilibrium, and the thermal relations of chemical action are all, taken in succession, based upon the recognition of equivalents, — electrical, chemical, thermal. The thermal equivalents suggest individual masses or mass-units of the elements in chemical action. Symbols are developed to express these mass-units, and the idea of valence follows. The conception of the molecule grows out of consideration of the volume occupied by the gram-equivalents of gaseous substances.

Only in the final chapter of this part is the notion of the atom introduced, with the molecule in its relations to the atom; and here are discussed also, as matters of theory, the molecule in the light of the kinetic theory of gases, the spatial relations of Van't Hoff and of Werner, some of the phenomena of solution, the electrolytic theory of dissociation, and the modern conceptions of ions.

PREFACE

In Part II the discussion of the properties of elements and their compounds is taken up in accordance with a modification of Mendeléeff's Periodic System, which facilitates, as it seems to us, orderly treatment. Graphic symbols, explained as simply diagrammatic, are used freely, in the conviction sustained by long experience that the student rarely misinterprets the real function of these valuable contrivances for coördinating facts. The ionic terminology has been employed, and the function of ions as parts of compounds and units of reaction is pointed out. We have not thought it desirable, however, to make use of the extreme developments of the idea of free ions. A good deal of care has been taken with the introductions to group characteristics, and with the summaries covering relations in detail.

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PART I — INDUCTIVE

CHAPTER I

CHEMICAL CHANGE AND THE CHEMICAL ELEMENTS

Properties of Substances. All material things, or substances, are alike in that all occupy space and all have weight. Substances differ, however, in behavior, or, as we say, in their *properties*.

Water and Iron. Water and iron are different substances. Each occupies space and each has weight, but each is different from the other and is possessed of peculiar properties.

Under ordinary conditions water is a liquid, while iron is a solid. When equal volumes or the spaces filled by each are considered, water is lighter than iron, and iron is heavier than water. Exposed to light, water is colorless and transparent, while iron is gray, opaque, and lustrous. When heated or deprived of heat throughout the small limits of ordinary temperature, water and iron simply expand or contract, each at its own rate. At a temperature moderately raised water boils and becomes gaseous, while iron remains solid far above red heat, only melting at very high temperatures, becoming gaseous at still higher temperatures. Upon cooling, liquid water freezes and becomes ice, while iron is unchanged in form, being merely contracted somewhat in volume by the same change of temperature. Water conducts electricity scarcely at all, while iron is a good conductor. Water is not made magnetic by proximity to electric currents, while iron, surrounded by a coil of insulated wire, is a magnet so long as the electricity passes through the wire, and becomes ordinary iron again when the current is broken. Water contained in a cylinder closed by a sliding piston is gaseous steam or liquid water at a temperature of 100°, according to the pressure put upon the piston or the force used to pull out the piston, the steam being condensed to water by sufficient mechanical energy, and the water gasified to steam by release of pressure or withdrawal of mechanical energy, while iron is practically unchanged under similar conditions.

Energy. Because of these marked differences in their properties we recognize water and iron as different substances; and we see, at the same time, that these properties of water and iron are brought out and varied by certain agencies — viz., light, heat, electricity, and mechanical energy — which, because they do work, we call forms of *energy*.

Identity. In order that use may be made of the properties of a substance for purposes of identification, it is first necessary to know what the properties of the substance are under definite conditions of energy. We have no difficulty in identifying iron or water by the assemblage of properties which each shows under the conditions of ordinary life, and this is because we have become familiar with the properties of iron or water under ordinary conditions. When water is heated under the atmospheric pressure, it boils, and passes as steam into the gaseous condition, and develops a new set of properties. To fully identify as water a specimen of gaseous material presented for identification, it becomes necessary to know the peculiar properties which are characteristic of water when it exists under the definite conditions of temperature and pressure of the new substance. *In general, a substance is identified when it exhibits a definite assemblage of properties under defined conditions of energy.*

Change of Condition. Every change of condition with respect to energy affects in some degree the properties of a substance, but some changes affect the totality of properties so little as not to change in marked degree the identity of the substance. A piece of iron raised from the ground is still iron, though by raising it we have expended energy upon it. A copper wire remains copper, though we change its properties somewhat while sending an electric current through it. A piece of cold silver when placed in the sunlight grows hotter, but most of its properties are slightly or not at all changed; it is still what it was in most respects, and, when cooled to its former temperature, is exactly what it was originally in all its properties. We do not consider that the iron, the copper, and the silver have undergone any essential change of identity.

Change of Identity. Many substances may be set in motion, submitted to pressure, acted upon by light or heat, electrified or magnetized, and in general may undergo simple changes of condition, which do not involve important changes of properties or relations to other substances, without losing their identity. The phenomena of change exhibited by matter are, however, often very far-reaching and complex, and it is sometimes very difficult to draw the line between changes of condition merely and changes of identity. We may choose, however, examples of such changes that are fairly typical. If we put a platinum wire into the colorless flame of a Bunsen burner, it becomes very hot, and glows with brilliance; when it is withdrawn from the flame, it cools in the air and proves to be the identical platinum that went into the flame — bright, untarnished, and to all appearances unchanged. While it is subject to changed conditions, it shows new properties, but when the original condition of temperature is restored, it is the same as before. There is no evidence to show that even during the altered condition the identity of the platinum was changed.

On the other hand, if we treat similarly a piece of polished magnesium wire, like the platinum in general appearance, we meet with different phenomena. The metal first simply melts, then burns in the air, gives out intense light, and is converted into a white powder, which, quite unlike the original metal in every particular, does not assume on cooling the aspect or properties of the metal. The change which affected the magnesium was at first one of condition merely, but soon became sufficiently far-reaching to affect the identity of the magnesium.

Chemical Changes: Chemistry. *Changes which affect the identity of substances are chemical changes, and chemistry is that branch of physical science which deals with the identity, and especially with changes in the identity, of substances.*

Effect of Heat upon Water. Certain changes which may be brought about in water likewise serve to illustrate the distinction between changes of condition and changes of identity. When we heat liquid water, it becomes hotter without changing its properties very much until it boils; then it becomes steam and is gaseous. If we cool the steam, liquid water is reproduced. Many of the properties of steam are different from those of liquid water, and some are closely similar, as we shall see when we come to study the relations of liquid water and steam to various other substances. So a difference of opinion might easily arise as to whether the changes which take place when liquid water is converted into steam, and steam back again into liquid water, are sufficient to change what we call the identity of the substance. The case is similar when we consider the change which takes place when liquid water freezes to form ice, which, in turn, is easily melted to reproduce the liquid water. Because, however, liquid water, steam, and ice are so easily and completely convertible into one another, and more especially because, as will appear when we study them in detail, they possess in common certain specific and very important relations to other substances, it is generally considered that they are the identical substance in different states or conditions; they are liquid, gaseous, and solid water.

Effect of Electricity upon Water. The case is different when we consider the effect of transmitting through water an electrical current. Pure water resists the passage of very powerful currents of electricity, but water acidulated with sulphuric acid conducts currents of low intensity, and is very markedly changed, the acid remaining unchanged at the end of the operation. An ordinary battery of three or four cells is sufficient for our purpose, and if we connect with the plates of such a battery strips of platinum foil, and dip them into water containing one ninth of its volume of sulphuric acid, itself without action upon the platinum, we have at each platinum electrode a brisk evolution of gas which may be collected and examined.

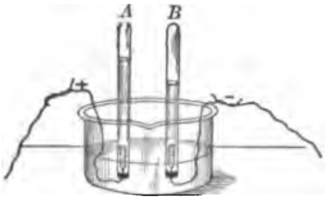

FIG. 1. — Action of Electricity upon Water.

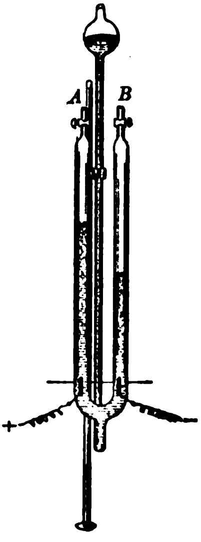

FIG. 2. Hofmann's Apparatus.

An apparatus devised by Hofmann especially for this purpose consists of two graduated tubes, set vertically, provided with stopcocks at the top, and uniting at the bottom in a common reservoir, and fitted near the bottom with platinum electrodes each joined to a platinum wire fused into the side of the tube. A simpler apparatus, answering the purpose sufficiently well, may be improvised from two test-tubes, two platinum electrodes, with insulated connecting wires, a dish of acidulated water, and two adjustable lead rings to weight and hold upright the test-tubes, first filled with the acidulated water and inverted over the electrodes in the acid. Upon examining the gases evolved at the electrodes, we find that the gas evolved from the negative electrode, joined to the corroded plate, is colorless, and is inflammable when approached by a lighted match as it issues into the air, and that a mixture of the gas with air explodes when lighted; while that developed at the positive electrode, joined to the uncorroded plate, is colorless and uninflammable, but makes a bit of wood, kindled to a spark, glow brightly.

Hydrogen and Oxygen. These gases evolved from water are obviously both very different from water in any of its states. Neither gas becomes liquid at any temperature at which water is liquid. The one gas burns when ignited in air, the other gas does not itself burn, but supports the combustion of a bit of kindled wood, while gaseous water possesses neither of these properties. If we were to extend very widely our comparison of the properties of these substances, especially in relation to other substances, we should find many points of difference and few resemblances. It appears that the new gases are not identical with the water from which they came, nor with one another. The *electrolysis*, or change under the action of the electric current, which water undergoes, is a typical chemical change. We recognize the fact that from water, which we know ordinarily as liquid at atmospheric temperature and pressure, two new gaseous forms of matter, each endowed with its own peculiar properties, have been produced. The inflammable gas we call *hydrogen;* the gas which will not burn, but which supports the combustion of the kindled wood, is *oxygen*.

Quantitative Study. Thus far in our study of the chemical changes which matter undergoes we have paid no attention to the amounts of matter involved. We cannot, however, acquire full knowledge of the change which has taken place in the water without determining the quantities of matter which are concerned in the change. The failure to follow the quantities of matter involved in chemical changes blocked the pathway of the early investigators, until Antoine Lavoisier, a French chemist, emphasized the advantage of quantitative methods, and laid firmly the foundation of modern chemistry.

Mass and Weight. The quantity of matter in a substance, or the *mass* of a substance, is most readily measured by its *weight;* for, though the weight of a substance is a variable quantity as we move the substance from place to place, — inasmuch as weight is dependent upon the intensity of the force of gravitation, or the attraction of surrounding matter, — the weights of any two substances compared at the same place must be proportional to their masses. The process of weighing upon the ordinary beam balance consists simply in counterpoising equal masses of matter upon the opposite pans of the balance, the equilibrium of which must remain unchanged by variations in the intensity of the force of gravity with change of locality, since such variations must affect both masses equally. Any chosen system of weights may be employed to determine relative masses, but for laboratory purposes the metric system of weights is in general use. Our unit of mass will be, therefore, a quantity of matter which will counterpoise a standard gram weight, and this is very nearly equal to the mass of one cubic centimeter of pure water in its densest condition at 4°.

Quantitative Electrolysis of Water. Now let us employ the balance to determine how quantity of matter is affected when water is changed into hydrogen and oxygen by the action of the electric current upon the acidulated water. In order to do this conveniently, we will make use of a compact form of apparatus which may be placed without difficulty upon the balance, and in which the two gases may be collected safely in mixture at the ordinary temperature.

Into a stout 500 $cm.^3$ flask put 100 $cm.^3$ of acidulated water, insert the stopper carrying the electrodes, and fasten it securely. By means of a tube connecting a vacuum pump to the tube passing through the stopper, exhaust the air from the flask and close the stopcock. Invert the flask and suspend the apparatus from one pan of a suitable balance capable of reading to milligrams or less, and counterpoise by weights or shot placed upon the other pan of the balance. Connect the battery wires with the elec-

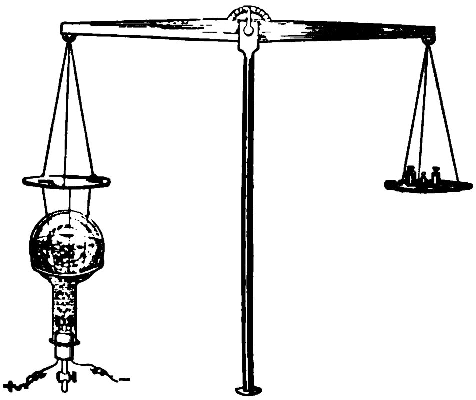

FIG. 3. — Quantitative Electrolysis of Water.

trodes and pass a measured current, taking care, with the fact in mind that an ampere of current produces about 10.5 cm.^{3} of the gas in one minute, to stop the action before the pressure of gas in the flask becomes too great; and then, disconnecting the battery wires from the electrodes, note the condition of equilibrium of the balance. If the operation has been conducted without leakage, it is found that the weight of the *system*, consisting of apparatus and inclosed matter, has suffered no change in consequence of the chemical change in which hydrogen and oxygen were evolved from water.

Similarly, if in burning the magnesium in air we were to carry on the operation in a sealed apparatus, containing the magnesium and air, and retaining the product of the burning, we should find that there is no change of weight involved in the chemical change which takes place when magnesium burns in air.

Conservation of Mass. Quantitative experiments like these just described may be made in other ways, upon a much larger scale involving greater masses of matter and employing more sensitive balances, with similar results. It is the testimony of all such experiments that *whenever we take into consideration all the substances entering into a chemical change and all the substances issuing from such a change, we find no evidence of change in the mass of matter under consideration.* This fundamental principle of chemistry was established by Lavoisier, in 1789, and is known as the *Law of Conservation of Mass.*

It is plain that in the production of two new substances, hydrogen and oxygen, from the single substance, water, without change of mass, a process of simplification has been going on, and that hydrogen and oxygen, both weighing together what the water from which they were derived weighed, and each, therefore, weighing less than the water, must be substances simpler than water. Our ability to trace the movement of masses of matter by use of the balance makes it possible to experiment still further with hydrogen and oxygen in search of substances still more simple, but by no process with which we are acquainted has a new substance of smaller mass, recognizable by the balance, been obtained from a given mass of either hydrogen or oxygen.

Heating of Mercury Oxide. Some other substances prove, like water, to be made up of simpler substances. If we shake a little red mercury oxide well down to the bottom of a hard glass tube closed at one end, counterpoise tube and contents upon a sensitive balance, then remove the tube, and heat it cautiously in a nearly vertical position at the lower end where the mercury oxide is, we note first a darkening in the color of the oxide, which, if we cool the tube without further heating, gives place to the original color of the mercury oxide. Thus far the change has been one of condition. Upon further heating, however, a very marked change takes place in the mercury oxide, and a little way up the tube, where it is cooler, a silvery mirror is deposited. Upon cooling the tube and placing it upon the balance, it is found that a loss of weight has taken place. The glass tube itself undergoes no loss of weight when heated by itself, so it must be supposed that the mercury oxide has lost weight in the process of heating. The residue in the tube, if the action has been carried to completion, is bright, lustrous, and consists of minute globules of mercury which may be united to form larger globules by pushing them together with an iron wire. The mercury, none of which has been lost from the tube if the upper parts are kept cool throughout, weighs less than the mercury oxide from which it was formed, and the loss of weight of the system is due, as we shall see later, to the parting of mercury from gaseous oxygen, which escapes. The mercury produced weighs less than the mercury oxide from which it came, and is evidently a substance simpler than mercury oxide.

Formation of more Simple Substances. The action of electricity in converting the complex water into the simpler substances, hydrogen and oxygen, and the action of heat upon the complex mercury oxide to liberate oxygen and form a residue of the more simple mercury, are both typical of many chemical changes in which substances are broken down into substances of smaller mass. *These are chemical changes in which complex substances become more simple.*

Heating of Copper in Air. Now let us consider, on the other hand, the chemical change which takes place when copper, heated in air, turns black, and becomes altered to copper oxide, a substance different from copper. Let us counterpoise carefully upon the sensitive balance a small porcelain crucible containing about 1 gram of clean copper, in a state of fine division, support the crucible with its contents on a pipestem triangle, heat it strongly for some minutes, exposed to the air, then cool and replace it upon the balance pan. It is evident at once that the weight of the system of crucible and the material in it has increased in the process of heating. Heat does not change the weight of the crucible by itself, but the material has changed in appearance and properties, and has increased in weight. Since the copper oxide is heavier than the copper from which it was formed, it must be a substance more complex than the copper. It appears that this increase in the weight of the system is due to the fact that something which we shall find later to be oxygen has been added to the copper from the air.

If we were to study similarly by the aid of the balance the burning of the magnesium in the air, in which the lustrous metallic magnesium is converted into a white powdery substance, we should find that the white substance which we call magnesium oxide weighs more than the original magnesium, showing that something has been added to the magnesium in the process of burning. The heavier magnesium oxide is more complex than the magnesium from which it was formed.

Formation of Complex Substances. The changes which copper and magnesium undergo when heated in air, resulting in the formation of substances which weigh more than the individual metals from which they were formed, are typical of many processes in which substances are added to one another to form substances of greater mass. *They are chemical changes in which simple substances become more complex.*

Chemical Elements. So we find that there are chemical changes in which substances become more simple, and chemical changes in which substances become more complex. It appears that matter can be added to matter with great readiness, to ever extending limits, but thus far it has been possible to push the simplifying of matter only to the limits of finding about eighty substances so simple that they have resisted all attempts toward further simplification. These substances we call the *chemical elements*, but it is highly probable that some of these so-called elements may be separable into still simpler forms of matter. This has been the experience in the past with many of the elements, and even now some of the elements are of doubtful character.

The following list contains the names of most of the substances which at present are considered to be elementary:

List of Elements.

Aluminium
Antimony
Argon
Arsenic
Barium
Bismuth
Boron
Bromine
Cadmium
Cæsium
Calcium
Carbon
Cerium
Chlorine
Chromium
Cobalt
Columbium
Copper

Erbium
Fluorine
Gadolinium
Gallium
Germanium
Glucinum
Gold
Helium
Hydrogen
Indium
Iodine
Iridium
Iron
Krypton
Lanthanum
Lead
Lithium
Magnesium
Manganese
Mercury
Molybdenum
Neodymium
Neon
Nickel
Nitrogen
Osmium
Oxygen
Palladium
Phosphorus
Platinum
Potassium
Praseodymium
Radium
Rhodium
Rubidium
Ruthenium
Samarium
Scandium
Selenium
Silicon
Silver
Sodium
Strontium
Sulphur
Tantalum
Tellurium
Terbium
Thallium
Thorium
Thulium
Tin
Titanium
Tungsten
Uranium
Vanadium
Xenon
Ytterbium
Yttrium
Zinc
Zirconium

Occurrence of Elements. Of the elements of this list a limited number, such as the gases of the atmosphere, some of the more common metals, and a few besides, occur free in the earth, but by far the greater number of elements are found naturally in association with other elements. It has been estimated that nearly one half of the entire mass of the earth is made up of the single element oxygen, that one quarter is silicon, and that oxygen and silicon together with aluminium, iron, calcium, carbon, magnesium, sodium, potassium, and hydrogen compose ninety-nine per cent. of the whole earth. Many of the elements are found in living tissues, carbon, hydrogen, oxygen, and nitrogen being particularly important as constituents of plants and animals.

Doubtful Elements. Some of the elements, such as the recently discovered radium and other constituents of rare minerals, are so seldom met with and so difficultly prepared in a state of purity that their properties have not been exhaustively determined, and the claims of some substances to be regarded as elements have not been fully considered. On the other hand, it is quite possible that some of the substances named in the list may some time be further simplified by ordinary chemical means, and so be elements no longer. Furthermore, it is quite conceivable that all the elements at present recognized may be composite, though not resolvable into simpler forms by ordinary means at our disposal, and this is a view which recent developments in the phenomena of radio-activity suggest.

Energy in Chemical Changes.

In the experiments which we have made, it has been obvious that *chemical changes are accompanied by changes in the energy of the system undergoing transformation.* The evolution of heat and light when magnesium burns, the development of electricity as the accompaniment of the chemical change which takes place in the electrical battery, the production of the mechanical energy of sound, and the motion which accompanies explosive action, are evidences of energy liberated in chemical change. Sometimes, however, energy disappears in a chemical change, as when heat is used up in simplifying mercury oxide, or when light affects the sensitive substances used in photography, or when electricity acts upon water without being converted into other common forms of energy.

We observe also that *conditions of energy play an important part in starting chemical changes.* In some of the experiments which we have made, it was necessary to provide energy from the outside continually in order that the reactions might continue, as in the action upon water of the electric current, the separation of the mercury and oxygen of mercury oxide, and the formation of copper oxide by heating copper in air. In some of our other experiments, however, it was only necessary to start the change by energy from the outside, the action once started proceeding steadily, as when we ignited a mixture of hydrogen and oxygen by heat or by the electric spark, or when we kindled magnesium in air. We may, however, pick out examples of chemical changes which proceed spontaneously, without accession of outside energy, as soon as the active substances come into close and intimate contact. Such are the production of clouds of ammonium chloride, floating as fine, solid particles, when gaseous hydrogen chloride and gaseous ammonia are allowed to mix; the bleaching of the colored solution of iodine by a solution of sodium thiosulphate in water, the two solutions being easily miscible; and the mutual action of sodium hydrogen carbonate and potassium hydrogen tartrate, which, though almost inert when mixed in solid condition, react when dissolved in water, with abundant evolution of gas.

Without going too deeply into this subject at present, we may recognize the facts that chemical changes may in some cases proceed spontaneously when substances capable of action under the existing conditions of energy enter the system and come into sufficiently intimate contact, or they may be set up at the expense of some one or other of the common forms of energy applied to the system from the outside; and that in the chemical changes energy may appear or disappear. To account for this appearance and disappearance of energy in the instances that have come to our notice, we have to recognize the existence of *chemical energy*, convertible into other forms of energy,—heat, light, electricity, mechanical energy,—from any one of which forms it may be produced, and into any one of which it may be changed.

CHAPTER II

COMPOUNDS, REACTIONS, AND CHEMICAL EQUIVALENTS

ALL known substances consist of one or more elements. We recognize, however, two very different modes according to which elements may be brought together. The association of elements may be such that the properties of the elements making it are simply added to one another, or such that the properties of the elements are merged and not simply added.

Mixture of Hydrogen and Oxygen.

Setting up the Hofmann apparatus once more and starting the current, we observe that the electrolysis of water gives us regularly a volume of hydrogen about twice as great as the volume of oxygen produced. Now let us so arrange the electrolytic cell that the hydrogen and the oxygen evolved in the decomposition of water may be collected in dry condition. We fill the apparatus so that the level of the liquid can never quite reach the open stopcocks, connecting to each stopcock a small drying tube, filled with calcium chloride, to keep back any water carried mechanically with the evolved gases, and joining to each of the dryers by means of a rubber connector a glass delivery tube of small bore. With the delivery tubes dipping beneath the surface of mercury contained in a shallow trough, the gases as they are evolved will bubble up through the mercury and may be collected conveniently in ordinary test-tubes filled with mercury and clamped with mouths above the ends of the delivery tubes and beneath the surface of the mercury. Upon starting the electric current, hydrogen collects in one tube while about half as much oxygen by volume rises into the other tube. When the one tube is partly filled with hydrogen we may move the tube containing the oxygen, still in vertical position, until it is close beside the tube containing the hydrogen, and then by carefully inclining it make some of the oxygen pass into the tube containing the hydrogen. When the oxygen and hydrogen are thus brought into contact at the atmospheric temperature, no change in properties is seen, and this is so whatever be the proportions in which the hydrogen and oxygen are associated.

Explosion of Mixture of Hydrogen and Oxygen.

When, for example, the gases are collected in a test-tube at the ordinary temperature in the proportion of two volumes of hydrogen to one volume of oxygen, the two gases exist in association without change of volume, density, color, or other obvious property. When, however, such a mixture is raised to a high temperature by bringing the mouth of the test-tube near a flame, a sharp explosion occurs, and water is deposited in the tube, apparently by union of the hydrogen and oxygen just evolved from water.

Union of Hydrogen and Oxygen in the Eudiometer.

The passage of an electric spark through a mixture of hydrogen and oxygen brings about a similar effect. For this experiment the mixed gases may be contained to best advantage in a stout graduated tube, known as a "eudiometer," the upper end of which is closed, while the lower end is effectively sealed by immersion in mercury contained in a shallow trough. The spark may be sent through the mixed gases between small platinum wires fused into the glass near the closed end of the tube in such a manner that the inner terminals will be opposite one another, but not in contact, while the outer ends of the wire may be readily connected in the secondary circuit of a small induction coil. The eudiometer is filled with mercury, inverted, and so placed that its mouth dips below the surface of the mercury in the trough. Hydrogen is introduced to a volume of 10 cm.^{3}, and 5 cm.^{3} of oxygen are added. The tube is clamped firmly with its mouth resting upon a rubber pad beneath the surface of the mercury. A spark is passed between the platinum electrodes by closing the secondary circuit of the induction coil, there is a flash of light in the tube, the gases disappear almost completely, and, inasmuch as the water produced occupies very little space, a partial vacuum is formed, and

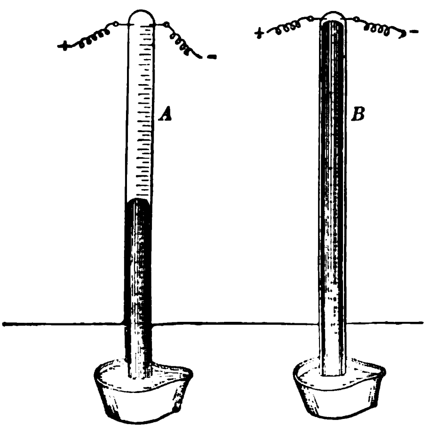

FIG. 4. — Union of Hydrogen and Oxygen in the Eudiometer.

mercury under the pressure of the air forces its way into the tube and nearly fills it. In this experiment the hydrogen and the oxygen existing in association have united to form water.

Compounds and Mixtures.

An aggregation of elements in which the characteristic properties of the elements composing it are merged and lost is called a *compound*, while an aggregation in which the component elements retain their individual properties is a *mixture*. Hydrogen and oxygen existing together in gaseous form at the ordinary atmospheric temperature constitute a mixture, and are said to be *mixed;* water, which has peculiar properties of its own, and in which the characteristic properties of hydrogen and oxygen are wholly lost, is a compound, and in water the hydrogen and oxygen are *united.*

We shall find, also, that compounds may sometimes enter into intimate association to form other more complex compounds in which the properties of the component compounds are lost; and here, too, we have the formation of new *compounds*. On the other hand, when compounds are associated without loss of their individual properties the resulting aggregation is a *mixture*. Black copper oxide and water, for example, both definite chemical compounds, may be mixed in any proportions without loss of the characteristic properties of either, but the pale blue substance known as copper hydroxide, which contains copper, oxygen, and hydrogen, and from which water and copper oxide may be obtained by heating, possesses properties quite different from the characteristic properties of either water or copper oxide, and is a new chemical compound.

Chemical Compounds.

So we may say more broadly that *a chemical compound is an aggregation the properties of which are characteristic and different from those of the component substances.*

The proportions in which the components of a mixture may be associated may vary widely, while the properties of the mixture vary proportionately and regularly. The proportions in which the components of a chemical compound are associated are subject to rule. Thus, in our former experiment with mercury oxide, a well-identified compound, it has been shown that mercury oxide is composed of the element mercury and a gaseous substance which escapes, and which we shall prove later to be the element oxygen. It has been found in repeating the experiment many times, that mercury oxide, whenever found and however made, is always composed of mercury and oxygen.

Simplifying Mercury Oxide Quantitatively. Now let us, by aid of the balance, repeat the experiment of simplifying mercury oxide, but this time quantitatively, so as to determine how much of a weighed amount of mercury oxide is mercury and how much is oxygen. Counterpoise carefully a hard glass tube of suitable size, closed at one end. Weigh out carefully 1 grm. of pure mercury oxide, put it into the tube, and counterpoise tube and substance upon a sensitive balance. Then remove the tube from the balance, and, inclining it slightly over a gas flame, heat it until the substance is completely volatilized from the bottom of the tube, while mercury has been condensed upon the wall of the tube higher up. Cool, replace the tube upon the balance, and determine the loss of weight.

When the experiment is very carefully performed with every precaution to insure accuracy, we obtain the following results:

Weight of mercury oxide taken . . .	1.0000 grm.
Weight of mercury remaining . . .	0.9260 grm.
Weight of oxygen escaping	0.0740 grm.

We find that 100 parts by weight of mercury oxide consist of 92.60 parts by weight of mercury united with 7.40 parts by weight of oxygen, and experience shows this to be true of mercury oxide within the limits of experimental error everywhere and at all times.

In the case of copper oxide, with which we have experimented before, and which we have made by heating copper in air, we find that it is always so made up that in 100 parts of it by weight, 79.90 parts by weight of copper are united with 20.10 parts by weight of oxygen; and blue copper hydroxide may be resolved by heat into water and copper oxide, 100 parts by weight of the copper hydroxide yielding 18.45 parts by weight of water and 81.55 parts by weight of copper oxide.

Constancy of Composition. As a result of many experiments upon many chemical compounds it may be said that *every well-characterized individual chemical compound always consists of the same elements united in invariable proportions by weight.* This generalization was made by Proust, a French chemist, in 1800, and is known as the *Law of Constancy of Composition.*

Chemical Reactions. Chemical changes involving the identity of individual substances, elementary or compound, are called chemical *reactions*, and the substances which enter the reactions are the *factors*, while the substances which come out are the *products*. Reactions are named and expressed according to the kind of change which they illustrate.

Analysis. *A reaction in which a compound is changed into simpler substances is a process of decomposition or analysis.* The change of the factor mercury oxide into the elementary products mercury and oxygen by heat is a process of decomposition or analysis, and may be expressed by the equation:

Mercury Oxide	=	Mercury	+	Oxygen
100 parts by weight		92.60 parts by weight		7.40 parts by weight

Similarly, the change of the compound copper hydroxide into the simpler compounds copper oxide and water is a process of decomposition or analysis, and may be stated in the equation:

Copper Hydroxide	=	Copper Oxide	+	Water
100 parts by weight		81.55 parts by weight		18.45 parts by weight

Synthesis. *A reaction in which elements or compounds unite to form more complex substances is a process of combination or synthesis.* The process in which the factors copper and oxygen unite to give the product copper oxide is a process of combination, or synthesis, and may be expressed by the equation:

Copper	+	Oxygen	=	Copper Oxide
79.90 parts by weight		20.10 parts by weight		100 parts by weight

We shall see also that compounds sometimes combine with one another in like manner to form more complex compounds.

Metathesis. *A reaction in which a substance is transposed from one compound to another is a process of metathesis.* For example, when a mixture of copper, 1 grm., with a suitable amount of mercury oxide, 3.4 grm., is heated in a glass tube closed at one end and nearly closed at the other, black copper oxide is left, while mercury volatilizes, and condenses on the wall of the tube. In this process oxygen leaves the factor mercury oxide and combines with the second factor, copper, to form the product copper oxide. The reaction is a metathesis, and may be expressed by the equation:

Mercury Oxide	+	Copper	=	Copper Oxide	+	Mercury
340 parts by weight		100 parts by weight		125 parts by weight		315 parts by weight

A metathesis obviously involves an analysis for one of the factors, and a synthesis for one of the products, in this case the mercury oxide undergoing analysis, and the copper oxide being formed by synthesis.

Sometimes, as we shall see when we become more familiar with chemical reactions, two compounds may react with one another in such a way as to undergo a double metathesis, involving the decomposition or analysis of both products, and the recombination of the resulting constituents to form two products by synthesis.

Definite Proportions. In accordance with the principle of constancy of composition of chemical compounds, all reactions of analysis, such as the decomposition of mercury oxide to mercury and oxygen, result in the breaking down of compounds of constant and definite composition into simpler substances of definite weight; in all reactions of synthesis, as in the formation of a definite weight of copper oxide from definite weights of copper and oxygen, definite weights of the factors combine to form a definite weight of product; and in all reactions of metathesis, as in the transfer of oxygen from mercury oxide to copper, definite weights of the factors combine to form definite weights of the products. So it follows as an observed and obvious consequence and corollary of the principle of constancy of composition of chemical compounds, that *individual substances, elementary or compound, reacting chemically, react in fixed and definite proportions by weight.* This principle is known as the *Law of Definite Proportions.*

Weights of Factors and Products. Now let us consider more particularly the relations by weight of factors and products in the reactions which we have studied. We have seen that 92.60 parts by weight of mercury are combined with 7.40 parts by weight of oxygen in 100 parts by weight of mercury oxide, and that 79.90 parts by weight of copper are combined with 20.10 parts by weight of oxygen to form 100 parts by weight of copper oxide. From these numbers we may find the proportions of mercury and copper, respectively, which will combine with the same fixed weight of oxygen, stated in grams or in centigrams or in terms of any convenient unit. It has been found by experience that the number 16 serves most conveniently to represent the fixed parts by weight of oxygen which enter into combination with various elements. Making 16 the fixed parts by weight of oxygen in mercury oxide, we find the parts by weight of mercury combined with oxygen in mercury oxide by solving the proportion:

$$7.40 : 92.60 = 16 : x. \quad (x = \text{nearly } 200.)$$

We learn from experiments made with the greatest care that 200 parts by weight of mercury are combined with 16 parts by weight of oxygen in making 216 parts by weight of mercury oxide.

Similarly, the parts by weight of copper combined with 16 parts by weight of oxygen are found by the proportion:

$$20.10 : 79.90 = 16 : x. \quad (x = 63.6.)$$

So it appears that 63.6 parts by weight of copper are combined in copper oxide with 16 parts by weight of oxygen to make 79.6 parts by weight of copper oxide. The expressions by which we represented the analysis of mercury oxide, the synthesis of copper oxide, and the metathesis between copper and mercury oxide may now be restated:

$$\begin{array}{ccccc} \text{Mercury Oxide} & = & \text{Mercury} & + & \text{Oxygen} \\ 216 & & 200 & & 16 \end{array}$$

$$\begin{array}{ccccc} \text{Copper} & + & \text{Oxygen} & = & \text{Copper Oxide} \\ 63.6 & & 16 & & 79.6 \end{array}$$

$$\begin{array}{ccccccc} \text{Mercury Oxide} & + & \text{Copper} & = & \text{Copper Oxide} & + & \text{Mercury} \\ 216 & & 63.6 & & 79.6 & & 200 \end{array}$$

Equivalent Proportions. The 200 parts by weight of mercury and the 16 parts by weight of oxygen hold one another mutually in combination in mercury oxide, and may be said to represent *proportions of mercury and oxygen equivalent to one another.* Similarly, the 63.6 parts by weight of copper and the 16 parts by weight of oxygen hold one another in combination in copper oxide and so represent *proportions of copper and oxygen equivalent to one another.* Furthermore, the 200 parts by weight of mercury and the 63.6 parts by weight of copper are the proportionate parts by weight which are capable of combining with 16 parts by weight of oxygen, and so they represent *proportions of mercury and copper equivalent to one another.* Of this last reaction we may also take another view. We may say that 63.6 parts by weight of copper are equivalent to 200 parts by weight of mercury because 63.6 parts of copper can replace 200 parts of mercury from combination with 16 parts of oxygen, and the 200 parts of mercury are equivalent to the 63.6 parts of copper by which they are replaced.

As we get on we shall see that 200 parts by weight of mercury, and 63.6 parts by weight of copper are capable of *combining* with fixed weights of elements other than oxygen, of *replacing* one another or of *being replaced* by one another in combination with such elements, and for that reason also 200 parts of mercury and 63.6 parts of copper must represent equivalent proportions of these elements; while the fixed weight of that element which is capable of combining with, replacing, or being replaced by 200 parts of mercury or the 63.6 parts of copper — and so of combining with 16 parts of oxygen, or of replacing 16 parts of oxygen from its combinations with these weights of mercury and copper respectively, or of being replaced from such combination by 16 parts of oxygen — will represent a proportion of that element equivalent to 16 parts of oxygen, 200 parts of mercury, and 63.6 parts of copper.

Equivalents of Elements. It is evident now that we may establish a system of *equivalents* which shall represent the proportionate weights of the elements — mercury, copper, and oxygen — in the reactions studied, or the proportions by weight in which these elements combine with one another, replace one another, or, in general, enter into reactions with one another. If in such a system we place the equivalent of oxygen at 16, the equivalent of copper will be 63.6 and the equivalent of mercury will be 200. In general, we may make the definition that *in a compound consisting of two elements the equivalent of an element is the weight of that element which will combine with, replace, or be replaced by either 16 parts by weight of oxygen or that weight of some other element which is capable of combining with, replacing, or being replaced by 16 parts by weight of oxygen.*

It must be noted, however, that the equivalent of an element, though invariable in a given compound of two or more elements, is not necessarily the same in another compound of the same elements. Thus in carbon dioxide the equivalent of carbon is always 6, while in carbon monoxide it proves to be 12, oxygen being 16. This is a matter to which we shall return.

Equivalents of Complexes and Compounds. As we proceed it will be found that in many chemical reactions occasions will arise for the discussion of the relations of compounds containing more than two elements, so that we shall have to deal with given *complexes* or aggregations of elements, such for example as the complex of hydrogen and oxygen in copper hydroxide. In a reaction involving such a complex *the weight of the complex which is involved in the chemical change with the equivalent of an element is the equivalent of the complex.* Moreover, since a definite weight of a compound contains elements and complexes of elements in definite weights, it is reasonable to extend the use of the term equivalent, and to postulate that *that weight of a compound which contains an equivalent of any chosen element or complex is an equivalent of the compound.*

Common Equivalents. The following table contains some equivalent weights, or equivalents, of elements and of compounds with which we shall meet in the reactions to follow, and which are in common use.

COMMON EQUIVALENTS

ELEMENTS

Bismuth	139.0	Nitrogen	28.08 14.04 9.36 7.02 5.62
Calcium	40.1		
Carbon	12.00 6.00		
Chlorine	70.90		
Copper	63.6	Oxygen	16.00
Hydrogen	2.015	Potassium	78.30
Magnesium	24.36	Sodium	46.10
Mercury	200.0	Sulphur	32.06
		Zinc	65.4

COMPOUNDS

Bismuth trioxide	465.00	Potassium chloride	149.20
Calcium oxide	56.10	Sodium chloride	117.00
Carbon dioxide	44.00	Zinc chloride	136.30
Copper oxide	76.60	Bismuth nitrate	789.24
Hydrogen oxide (water)	18.02	Bismuth hydroxynitrate	609.12
Mercury oxide	216.00	Nitric acid	126.10
Nitrogen pentoxide	108.08	Potassium nitrate	202.38
Zinc oxide	81.40	Sodium nitrate	170.18
Calcium hydroxide	74.12	Sulphuric acid	98.08
Potassium hydroxide	112.32	Magnesium sulphate	120.42
Sodium hydroxide	80.12	Potassium sulphate	174.36
Zinc hydroxide	99.42	Potassium hydrogen sulphate	272.44
Hydrogen chloride	72.92	Calcium carbonate	100.10

CHAPTER III

HYDROGEN

Reaction of Magnesium with Sulphuric Acid.

We have seen that hydrogen may be produced with oxygen by the electrolysis of water. As we experiment further we find that hydrogen may be evolved from some substances other than water.

Let us try the effect of putting a small piece of magnesium into a test-tube containing a little dilute sulphuric acid. Instantly we note an effervescence which suggests the liberation of some form of gaseous matter into the atmosphere, and finally the entire disappearance of the metal. In this experiment the liquid remains clear, nothing is thrown down in solid form; but if after the action is over we take pains to evaporate the liquid by heat, a white solid substance known as magnesium sulphate is left, from which by appropriate chemical means the exact amount of magnesium taken can be recovered.

Preparation of Hydrogen from Magnesium and Sulphuric Acid.

If we repeat the experiment with a little change in the mode of manipulation, we shall be able to collect the gas evolved and to test it. So let us fill a test-tube with water, containing about a thirtieth of its volume of sulphuric acid, cover the test-tube tightly with the thumb, and inverting it, stand it in a dish containing the same mixture of acidulated water, with its mouth below the surface of the liquid in the dish. A collar made of a strip of sheet lead slipped over the tube holds it erect when left alone. Introduce a bit of magnesium into the slightly inclined tube in such a manner that no air may enter. The gas evolved remains in the tube unless there is more than enough to displace the water entirely. It is evidently colorless, and, when we remove the tube from the dish, first closing the mouth of the tube with the thumb, proves to be odorless if it is pure. When a second portion of the gas, prepared and collected in the same manner, is ignited, it burns with a nearly colorless flame. The properties of this gas prove upon further careful examination to be identical with those of hydrogen produced in the electrolysis of water. *The action of magnesium upon dilute sulphuric acid has produced hydrogen.* The reaction may be expressed by the equation:

Magnesium + Sulphuric Acid = Magnesium Sulphate + Hydrogen

Preparation of Hydrogen from Zinc and Sulphuric Acid.

To prepare hydrogen on a larger scale advantage is taken of the fact that zinc, which is less expensive than magnesium, acts similarly upon sulphuric acid, with the production of hydrogen. A convenient form of apparatus for generating and collecting the gas consists of a flask holding about 250 cm.^{3}, and fitted with a rubber stopper perforated with two holes, through one of which passes tightly a safety funnel-tube, and through the other a delivery tube. Granulated zinc is introduced into the flask, the stopper and tubes are adjusted, water is poured into the flask until the lower end of the safety tube is submerged, a few drops of a solution of copper sulphate are introduced, to cover the zinc with a slight coating of copper, thus making an electric couple in which the zinc is more sensitive to acid, and sulphuric acid is added cautiously, and mixed with the water by gentle agitation of the flask, until the evolution of gas is rapid and regular. If the supply of gas slackens, it may be increased by further addition of dilute sulphuric acid, until the zinc is exhausted. The first portions of gas escaping are, of course, chiefly air, but after a little time the hydrogen is delivered in fairly pure condition. Upon evaporating the liquid remaining after the zinc has ceased to act upon the sulphuric acid a white substance, zinc sulphate, is obtained. The reaction of zinc and sulphuric acid proceeds according to the equation:

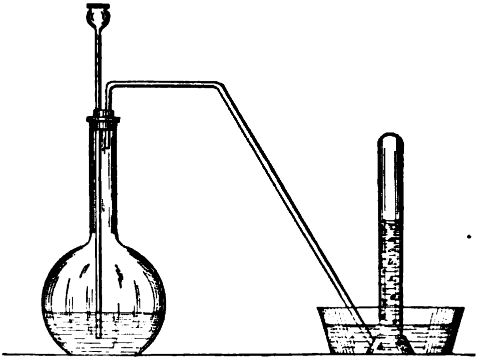

FIG. 5.— Preparation of Hydrogen.

Zinc + Sulphuric Acid = Zinc Sulphate + Hydrogen

Kipp Generator. For the continued generation of hydrogen in considerable quantities we may find it convenient to use an apparatus devised by Kipp, which consists of three chambers. The uppermost chamber is extended in a tube which fits tightly into the middle chamber and passes loosely through the constriction between the middle chamber and the lowest chamber nearly to the bottom of the apparatus. A delivery tube, fitted with a stopcock, leads out of the middle chamber. We place a sufficient quantity of granulated zinc in the middle chamber, adjust the delivery tube, and then pour dilute sulphuric acid into the upper chamber until the lower chamber is filled, and the acid comes into contact with the zinc in the middle chamber. A brisk evolution of hydrogen is now set up, which will continue as long as zinc and sulphuric acid remain, or until the stopcock in the delivery tube is closed, in which latter case the continued evolution of gas forces the acid off from the surface of the zinc and stops the action until the stopcock is again opened.

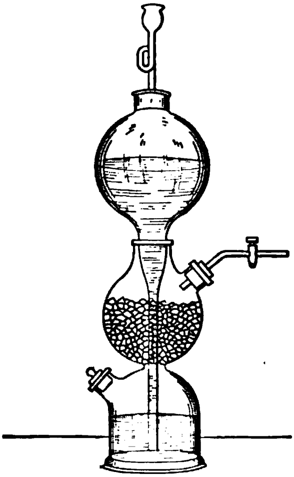
FIG. 6.— Kipp Generator.

For collecting the gas a simple form of *pneumatic trough* may be easily constructed of two pans of tin plate, varnished with asphalt. The larger one holds water, and the smaller pan, perforated on its side and bottom, and inverted, serves as a support for the test-tubes to serve as gas receivers. The vessels for holding the gas are weighted with lead rings to give them stability, and having been previously filled with water, are placed in succession, mouth downward, over the central hole in the smaller pan which is submerged beneath the water to a convenient depth. The gas is delivered to the interior of the smaller pan through the side perforation and rises into the tube placed to receive it, at the same time forcing the water from the receiving vessel downward into the larger pan. In this manner several tubes may be filled with hydrogen and set aside for examination.

If we remove one of these tubes containing hydrogen from the trough, having first stoppered it with the thumb, and apply a flame

Burning of Hydrogen in Air. to the mouth of the tube, the same nearly colorless flame appears which we saw when we burned the gas which was produced in the electrolysis of water, and by acting with magnesium upon sulphuric acid. *When the hydrogen is mixed with air before the application of flame the combustion takes place explosively throughout the mixture*, and by taking pains to make various mixtures of hydrogen with air it may be readily shown that *the explosion is most violent when two sevenths of the volume of the mixture is hydrogen and five sevenths air* — a fact for which we shall find an explanation later.

Explosion of Hydrogen and Air. A convenient way to get any desired mixture of hydrogen and air is to introduce into a test-tube filled with water the proper amount of hydrogen, and then by cautiously inclining the tube at the level of the water in the pneumatic trough to allow air to enter safely, and gradually to mix with the hydrogen. It is plain that, in order to avoid dangerous explosions, the greatest care should be taken never to bring a flame near the gas escaping from a hydrogen generator in action until it is certain that the gas is delivered in sufficiently pure condition to be inexplosive. The pure gas may be burned safely as it issues from a small jet attached to the generator, and a convenient test of purity is to fill a tube with the gas and see if the small portion thus collected burns quietly when inflamed.

Lightness of Hydrogen. Let us vary a little the manipulation of the experiment in which we remove from the trough a tube filled with hydrogen and apply the flame. Let us this time simply pick up the tube containing hydrogen without taking pains to close it, and carry it mouth downward to a flame. We find that the hydrogen remains in the tube and burns quietly. It would seem that the air does not rise at all rapidly into the tube to replace the hydrogen. Take another tube from the trough, hold it mouth upward, and then bring it to the flame. This time there is no gas to inflame in the tube; it has escaped. Now take a third tube of hydrogen from the trough, holding it mouth downward, slowly and carefully invert it under and close to another tube held vertically with its mouth downward, and then after an interval of half a minute apply a flame to the mouth of each. If the experiment has been conducted properly, the gas in the tube which formerly held the hydrogen, now held mouth upward, does not ignite, while the gas in the tube held mouth downward and uppermost explodes when the flame approaches it. Evidently we have been able to pour the hydrogen gas upward, displacing the air from the upper tube to make room for it. We may illustrate the lightness of hydrogen in a still more striking manner by suspending from one arm of a balance, and counterpoising, a large inverted beaker, and then bringing under the beaker a cylinder, mouth upward, containing hydrogen. The hydrogen will rise rapidly from the cylinder into the beaker, as is evidenced by the disturbance of the equilibrium of the balance. The conclusion that hydrogen is lighter than air is obvious. Indeed, hydrogen is the lightest form of matter known to exist. By most careful investigation it has been found that *1 liter of hydrogen at 0° and under 760 mm. pressure (at sea level, latitude 45°) weighs 0.0899 grm.*

Effect of Hydrogen on Combustion. We have found out that hydrogen is colorless, odorless, and is combustible in contact with air, and that it is very light as compared with an equal volume of air. We have yet to test its behavior toward other combustibles — to see whether it will support the combustion of substances which burn freely in air. This matter may be easily put to trial by taking from the trough another tube of hydrogen, and, while holding it mouth downward, introducing from below a small lighted taper. The gas inflames at the mouth of the tube, but the taper as it passes upward into the hydrogen is extinguished, to be rekindled as it is withdrawn through the hydrogen still burning on its surface of contact with the air; and this process of extinguishing the taper by putting it into the hydrogen and relighting it by returning it through the flame into the air may be repeated, if the tube is large enough, several times. The taper is typical of other substances which burn in air. It has been found by experiment that substances which burn in air, and which are commonly called combustible, do not burn in hydrogen. *Hydrogen is itself combustible, but does not support combustion of ordinary combustibles.*

Formation of Water by burning Hydrogen. In these experiments we have been handling hydrogen collected over water, and so have been led to overlook a most important fact. If, as in a former experiment with hydrogen produced in the electrolysis of water, we take the precaution to attach to the generator a tube filled with calcium chloride, a substance without action on hydrogen but possessing a great attraction for water, we may insure the dryness of the hydrogen, and if we connect the end of this *drying tube* with a glass tube bent in a right angle, it is possible to fill tubes with dry hydrogen by the downward displacement of the air. It is best in this process to insert the delivery tube to the extreme end of the test-tube, held vertically with its mouth downward.

When a dry test-tube, filled with hydrogen that has been rendered dry by this process, is brought to a flame, and slowly inverted, so that the resulting flame of burning hydrogen may travel the entire length of the tube, close observation will reveal the deposition of moisture on the walls of the tube; the same deposition of moisture may be observed when a mixture of dry hydrogen and air is exploded in a tube; and if the dry, pure hydrogen is ignited as it issues from the generator and allowed to burn inside a tall, dry glass chimney or flask, the production of moisture is very obvious. *This moisture is water, and water, or hydrogen oxide, which as we have seen is a compound of hydrogen and oxygen, is produced by the burning of hydrogen in air.* This fact, first observed by Henry Cavendish, of England, gives the reason for assigning to the element the name Hydrogen, formed from two Greek words, meaning "water" and "I produce." Hydrogen is the water producer.

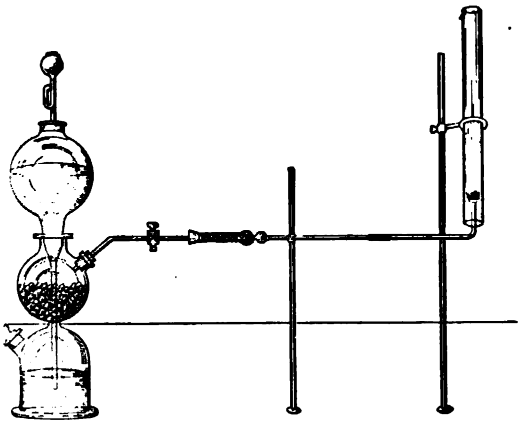

FIG. 7.—Formation of Water by burning Hydrogen in Air.

In this experiment we have incidentally the proof of the fact, previously stated only, that air contains oxygen. When the hydrogen burns in air to form water, it simply combines with oxygen contained in the air.

Hydrogen + Oxygen = Hydrogen Oxide

Weight of Hydrogen evolved by 0.1 grm. of Magnesium. We have found that the metals magnesium and zinc are capable of producing hydrogen from sulphuric acid. It is natural for us next to inquire, How much hydrogen may be replaced in sulphuric acid by a given weight of magnesium or of zinc? Or, in other words, what are the fixed and definite proportions by weight in which these metals and hydrogen are involved in these particular chemical changes? We may answer this question by acting upon a known weight of either metal with an excess of sulphuric acid, and either noting the weight of hydrogen evolved, or measuring its volume at any given temperature and pressure, and then calculating its weight.

Let us first determine by experiment what weight of hydrogen may be replaced in an excess of sulphuric acid by 0.1 grm. of magnesium. It is extremely difficult to collect, and either weigh or measure directly, so light a body as hydrogen, and for this reason we will devise a method for determining indirectly the weight of the hydrogen evolved. A very simple apparatus enables us to accomplish this result with a fair degree of accuracy. Two little flasks *A* and *B*, each of about 50 $cm.^3$ capacity, are dried and fitted with rubber stoppers, each perforated with two holes. Each flask is provided with a short, straight glass tube, fitting closely and just passing through one of the perforations in the stopper. A glass tube, bent twice at a right angle, connects the interior of the two flasks, reaching from about 1 cm. below the neck of *A* nearly to the bottom of *B*. The first flask *A* furnishes a chamber in which the reaction between magnesium and sulphuric acid may take place, and the second flask *B* serves to contain a quantity of sulphuric acid, from which a small amount may be drawn into *A* to effect the desired reaction, while the remainder of the acid, still contained in *B*, will, by absorption, prevent moisture from leaving the apparatus during the course of the experiment. Care should be taken to see that the end of the bent tube through which the sulphuric acid is drawn into *A* shall be so much lower than the end of the straight tube that there shall be no danger of acid getting into the straight tube.

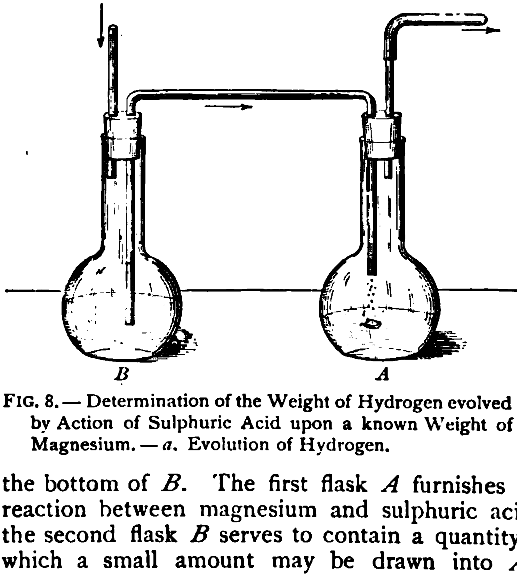

FIG. 8. — Determination of the Weight of Hydrogen evolved by Action of Sulphuric Acid upon a known Weight of Magnesium. — *a*. Evolution of Hydrogen.

Let us, then, put enough water into *A* to fill it to a depth of about 1.5 cm., and into *B* let us pour strong sulphuric acid to a depth of about 2 cm. Weigh out carefully about 0.1 grm. of clean magnesium ribbon, and put it into *A*. Place the two stoppers, containing the short straight tubes, and connected by the bent tube, securely into the necks of the two flasks, taking care to see that all joints are tight, and that the connecting tube reaches only to the neck of *A*, and nearly to the bottom of *B*. Now counterpoise very carefully this whole apparatus upon a balance capable of indicating milligrams or less. While, for this purpose, a sensitive balance of precision is best, with careful manipulation an ordinary hand scale, provided with a pointer to indicate slight variations from a condition of equilibrium, will serve fairly well. Let us suspend the apparatus, properly arranged, across one of the pans of such a hand scale, and add weights to the other pan until the oscillations of the pointer indicate very exactly the condition of equilibrium.

Then, leaving the counterpoising weights on the scale, remove the apparatus, attach a small rubber suction tube to the straight tube of *A*, which contains the magnesium and water, and very cautiously draw a little of the sulphuric acid from *B* over into *A*, instantly closing the end of the straight tube of *A* with a rubber cap, made by closing with a bit of glass rod one end of a short piece of small rubber tubing. The acid mixes with the water in *A*, and acts upon the magnesium with liberation of hydrogen, which can escape only through *B*. The strong sulphuric acid in *B* has a powerful attraction for water, and for this reason it retains any traces of moisture which may be carried over mechanically with the escaping hydrogen, and thus prevents any loss of weight by loss of water. If the evolution of gas ceases before the magnesium has entirely disappeared, we must again transfer a little more acid from *B* to *A* in the same manner as before, and the operation must be continued until all evolution of hydrogen has ceased. The apparatus should now contain all the material originally contained in it except some of

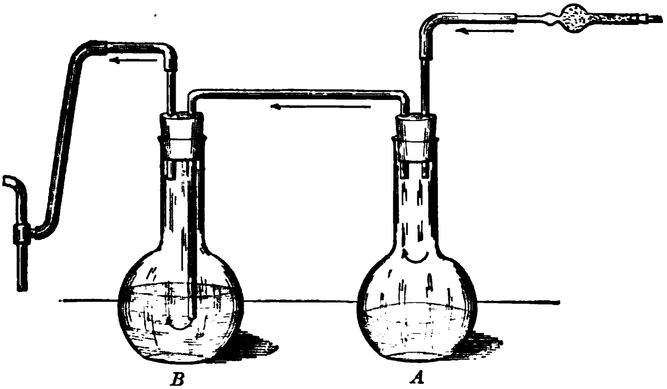

FIG. 9. — Determination of the Weight of Hydrogen evolved by Action of Sulphuric Acid upon a known Weight of Magnesium. — *b*. Removing the Hydrogen from the Apparatus.

the hydrogen evolved, and the greater part of the air originally present which has been forced out through the sulphuric acid.

A considerable amount of the evolved hydrogen, doubtless with some of the original air, must still be present in the two flasks. Such residual hydrogen should be readily removed by drawing a current of air from the outside through both flasks. Let us remove the cap from the straight tube of *A*, attach a drying tube, containing fused calcium chloride, in its place, to remove moisture from the external air as it is subsequently introduced into the apparatus, connect the straight tube of *B* with the suction tube, and draw air, best by means of an aspirating pump, through the flask for some minutes in order to replace the hydrogen entirely by air. When this is accomplished, the apparatus is in exactly the same condition as it was when first counterpoised upon the scale, except that the hydrogen liberated by the magnesium has been removed.

If we now replace the apparatus upon the scale pan, we are not surprised to discover that it is appreciably lighter than it was before. We have taken precautions to prevent the addition to the system of moisture or other external matter, excepting an amount of air just equal to that originally present, and we have been equally careful, while removing the last trace of liberated hydrogen, to guard against the escape of any matter other than hydrogen. We feel certain, therefore, that the loss of weight sustained by the system is equal, within the limits of experimental error, to the weight of the hydrogen set free from sulphuric acid by the magnesium. This weight we will determine by adding weights to the scale pan containing the apparatus until equilibrium is again established. Practically we find that 0.1 grm. of magnesium sets free approximately 0.008 grm. of hydrogen, or, in other words, 1 part by weight of magnesium sets free 0.08 parts by weight of hydrogen. Repeated experiments with the hand scale, in spite of our somewhat rough manipulation, should give fairly accordant results. When, however, we employ a delicate balance of great precision, and take every possible precaution to insure accuracy, *we find gravimetrically that 1 : 0.0827 is the fixed and definite proportion by weight in which magnesium and hydrogen invariably take part in the particular chemical change we have studied.*

Volume of Hydrogen evolved by 0.1 grm. of Magnesium.

The indirect determination of the weight of hydrogen replaced in sulphuric acid by 0.1 grm. of magnesium is accomplished somewhat more simply by measurement of the volume of hydrogen evolved. Fill with water, containing about a thirtieth of its volume of sulphuric acid, a flask of about 150 cm.^{3} capacity; fit a strip of sheet lead about the neck of the flask so that when the flask is subsequently inverted it will stand upright; put into a beaker of water about 0.1 grm. of magnesium ribbon, carefully weighed, and rolled up compactly; close the flask with the hand to prevent entrance of air, and inverting it, place the mouth of the flask directly over the magnesium, so that as the acidulated water mixes with the water in the beaker, and acts upon the magnesium, the hydrogen set free on the surface of the magnesium may all rise into the flask and be collected. When the magnesium has all disappeared, we have collected in the flask, by downward displacement of the acidulated water, the hydrogen which has been set free. It remains to determine the volume and then the weight of the hydrogen.

Law of Boyle.

The relation between the volume and the weight of any gas varies, as we know, with the temperature and pressure of the gas. According to the *Law of Boyle*, which is not absolute, but applicable with a high degree of accuracy to many gases for considerable variations of pressure, ***the volume of a definite weight of a gas at constant temperature is inversely proportional to the pressure.*** If the pressure is doubled, the gas is compressed to half the original volume; and if the pressure is halved, the volume is doubled. In general, if V and V' represent the volumes of a definite weight of gas under the conditions of pressure indicated by P and P', we have

$$V : V' = P' : P$$

and

$$V' = \frac{VP}{P'}$$

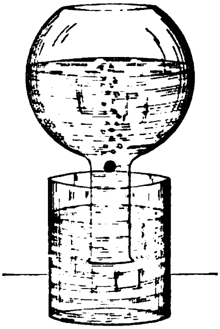

FIG. 10. — Determination of the Volume of Hydrogen evolved by Action of Sulphuric Acid upon a known Weight of Magnesium.

Barometer.

To measure the pressure of a gas we generally determine how high a column of mercury it is capable of supporting. If a tube of sufficient length and closed at one end be filled with mercury and inverted without admission of air, and so placed that its mouth is beneath the surface of mercury in an open vessel, the mercury sinks in the tube, leaving above its level a vacuum complete but for traces of mercury vapor, to such a point that the downward pressure of the liquid mercury due to gravity, and in very small degree by its vapor pressure, just balances the pressure of atmosphere upon the mercury in the dish. At the sea level the column of mercury thus supported stands on the average at 76 cm. or 760 mm. above the surface of mercury in the dish, but this *normal height* of the column, corresponding to the *normal atmospheric pressure* at the sea level, in latitude 45°, and at 0°, is subject to variations corresponding to the alterations in atmospheric pressure which accompany changes of altitude in relation to the sea level, to weather changes and in slight degree to changes in latitude. The ordinary mercury *barometer*

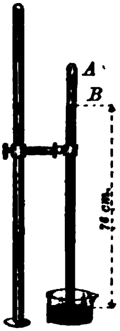

FIG. 11. — The Mercury Barometer.

which we use to measure air pressures is a simple graduated tube of convenient length, filled very carefully with pure dry mercury, inverted, and so arranged that a column of mercury is sustained within it by the pressure of the air upon the surface of the mercury which seals it.

Law of Charles. According to the *Law of Charles, the volume of a definite weight of a gas under constant pressure varies directly as the so-called "absolute temperature."* This is simply a uniform scale the zero of which is 273° below the melting point of ice, the zero of the centigrade scale, while 373° on the absolute scale represents the temperatures of water boiling under normal atmospheric pressure. Practically, we measure "absolute temperatures" by taking the observed temperatures of the centigrade scale and adding to them the number 273. If V and V' represent the volumes of a definite weight of gas at constant pressure under varying conditions of temperature, while T and T' represent the varying temperatures measured upon the absolute scale, then

$$V : V' = T : T'$$

and

$$V' = \frac{VT'}{T}$$

When a change of volume of a gas due to changing pressure, and a change of volume due to changing temperature, take place simultaneously, the new volume V' may be found from the expression

$$V' = \frac{VPT'}{P'T}$$

Now, returning to the case of the hydrogen obtained by the action of magnesium upon the dilute sulphuric acid, we may assume the temperature of the hydrogen to be the same as that of the liquid in the flask. Let us make the pressure under which the hydrogen is confined equal to that of the air outside by so placing the flask that the level of the liquid is the same within the neck of the flask and in the beaker. Holding the flask in this position, close the mouth of it with a glass plate, then quickly turn the flask mouth upward, determine the temperature of the liquid remaining in the flask, and then measure carefully the volume of this liquid. Now fill the flask to overflowing with water, cover it exactly with a glass plate, taking care that no bubbles of air shall be included, and measure the water contained in the full flask. The difference between the two measured volumes is the volume of the hydrogen measured under the prevailing conditions of temperature and pressure. We have determined with sufficient exactness the temperature of the hydrogen by observing the temperature of the liquid in the flask. To complete our data we have only to determine the pressure of the air, and consequently that of the hydrogen, by reading the height of the mercury in a barometric tube at the time and place of the experiment.

Calculation of Weight of Hydrogen from its Volume.

It is customary, in stating the volume of gas concerned in a chemical reaction, to give the volume which the quantity of gas in question will occupy under standard conditions, — that is at 0°, and under a pressure equal to that atmospheric pressure which supports a column of mercury 760 mm. high in latitude 45°. Suppose that in an experiment conducted in the manner described, 0.1 grm. of magnesium yielded 98.6 cm.^{3} of hydrogen, while the thermometer immersed in the water in the flask registered 16°, and the barometer stood at 759 mm. We are to ascertain the volume which the 98.6 cm.^{3} of hydrogen would occupy at 0°, under a pressure of 760 mm. at the sea level in latitude 45°.

Substituting for V in the formula given above the observed volume of hydrogen, 98.6; for P, the observed pressure, 759, disregarding as insignificant for our present purpose minor corrections of the observed height of the barometer; for P', the normal pressure, 760; for T, 16 + 273, the observed temperature on the centigrade scale increased by 273; for T', 0 + 273, the absolute temperature for 0°; we have,

$$V' = \frac{98.6 \times 759 \times (0 + 273)}{760 \times (16 + 273)} = 93.02 \text{ cm.}^3$$

We may say, then, that the hydrogen replaced in sulphuric acid by 0.1 grm. of magnesium will measure 93.02 cm.^{3} under standard conditions of temperature and pressure.

In order to find the weight of any given volume of hydrogen, it is only necessary to make use of the datum that 1 liter of hydrogen at 0° and 760 mm. at sea level in latitude 45° weighs 0.0899 grm., and that 1 cm.^{3} of hydrogen under the same conditions weighs 0.0000899 grm. Whence we have, for the special case in hand, *$93.02 \times 0.0000899 = 0.0084$ grm. as the weight of hydrogen replaced in sulphuric acid by 0.1 grm. of magnesium*, a result closely in accord with that obtained from our former gravimetric experiments. *By most carefully executed volumetric experiments, we find that 1 : 0.0827 is the fixed and definite proportion by weight in which magnesium and hydrogen take part in the particular chemical change we have studied.*

Were we to make similar experiments, using suitable weighed quantities of zinc instead of magnesium, *we should find 1 : 0.0308 to be the fixed and definite proportion in which zinc and hydrogen take part in the chemical change.*

When we shall have found the equivalent of hydrogen, these ratios, 1 : 0.0827 and 1 : 0.0308, will enable us to determine the equivalents of magnesium and zinc respectively.

CHAPTER IV

OXYGEN AND OXIDES

We have seen that the gas evolved at the negative pole of the battery during the electrolysis of water is hydrogen, while that liberated at the positive pole is in volume about half as great as the hydrogen, has properties quite distinctive from those of hydrogen, and is called oxygen. We have already studied hydrogen somewhat particularly, and we will now turn our attention to the other gas evolved in the electrolysis of water, *oxygen*.

Withdrawal of Oxygen from Air.

When hydrogen burns in air water is formed; in the decomposition of water hydrogen is recovered and oxygen is also liberated, and the inference that *oxygen is extracted from air by burning hydrogen* is plain. Investigation shows that *many other substances possess, like hydrogen, the power of withdrawing oxygen from air and combining with it to form compounds from which it is often possible by suitable means to isolate the oxygen in free condition.* The element mercury, for example, is such a substance, and when it is heated in air to a temperature a little below 357°, its boiling point, it slowly changes to a red powder, already familiar to us, which at a higher temperature is resolved again into mercury and oxygen gas. The combination of mercury with the oxygen of the air takes place but slowly, so that, when we desire to prepare oxygen from the red mercury compound, we find it more convenient to start with the compound ready made by another process.

Preparation of Oxygen from Mercury Oxide.

So let us proceed to fill a hard glass tube, about 1 cm. in diameter and sealed at one end, about half full of the red mercury oxide, fit to the open end a delivery tube, place the tube in a furnace consisting of a number of Bunsen burners set in line, dip the delivery tube beneath the surface of water in a pneumatic trough, and heat the tube to low redness. As the experiment progresses, oxygen is given off, and mercury condenses and collects in the cooler parts of the tube as we have also seen in an earlier experiment. When the air present at first is out of the tube, the gas collected is pure oxygen like that formed by the electrolysis of water, and, at ordinary temperatures and pressures, is colorless and odorless. *A liter of oxygen at 0° and 760 mm., at sea level in latitude 45°, weighs 1.4291 grm., so oxygen is 15.90 times as heavy as an equal volume of hydrogen under standard conditions.* When we apply a lighted taper to the mouth of a tube in which the gas has been collected, we see, as before, that the oxygen is incombustible itself, but aids greatly in the combustion of the taper. These characteristic properties of oxygen are always observable in that element, however it may be produced. It was by concentrating the sun's rays on mercury oxide by means of a burning glass that Joseph Priestley, of England, in 1774, prepared oxygen, so that this particular process possesses historic interest.

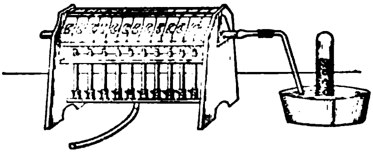

FIG. 12. — Heating Mercury Oxide.

Preparation of Oxygen from Potassium Chlorate.

A more practical method for the production of oxygen in considerable quantities consists in heating potassium chlorate, a substance very rich in oxygen, and collecting the gas liberated. The action is greatly facilitated by the presence with the potassium chlorate of an equal weight of manganese dioxide, which, though remaining at the end of the operation practically unchanged, yet serves a most useful purpose in enabling the oxygen to escape from the potassium chlorate at a temperature much lower than would be otherwise possible. Indeed, the evolution of the gas from the mixture proceeds so rapidly, when the action once begins, that it is wise to provide beforehand, filled with water and standing in readiness in the pneumatic trough, the glass vessels in which the gas is to be collected. It is well before the experiment to test the purity of the manganese dioxide and potassium chlorate employed by heating a small quantity of the prepared mixture of these substances in a test-tube. Care must be taken to guard against accidents which may result from too violent delivery of oxygen or clogging of the tubes. For the production of oxygen on a large scale metallic retorts and connections are preferable.

For the production of oxygen for demonstration, let us half fill a 30 cm.^{3} round-bottomed flask, made of hard glass, with an intimate mixture of equal quantities of powdered manganese dioxide and granulated or powdered potassium chlorate. Arrange the flask in a nearly horizontal position, and connect it with a delivery tube of large diameter. The connection, to guard against clogging of the delivery tube, is best made by tightly stretching a short piece of rubber tubing over both the delivery tube and the neck of the flask brought close together. To provide for the removal from the gas of solid matter which may tend to be carried over mechanically, arrange the delivery tube so that it reaches nearly to the bottom of a tightly stoppered *washing flask*, partly filled with water, and from the upper part of the flask arrange another tube to carry away the purified gas. Heat the generator flask and contents very gradually with an open flame, held conveniently in the hand. When the evolution of oxygen becomes rapid and regular the flame need be no longer employed, and when the evolution entirely ceases the delivery tube should be immediately removed from the washing flask to prevent the drawing up of water into the generator flask while the latter is cooling.

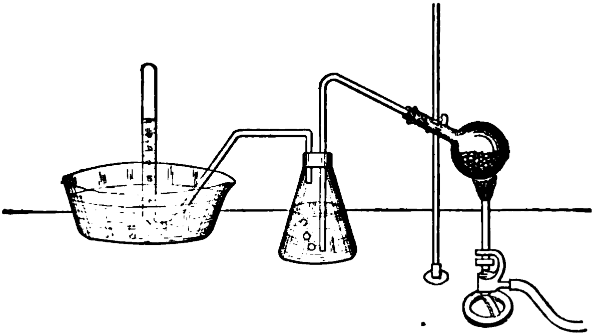

FIG. 13. — Heating Potassium Chlorate and Manganese Dioxide.

Burning of Substances in Oxygen. With an abundant supply of oxygen, contained conveniently in covered glass cylinders, we may extend our experimentation to the study of the behavior of combustibles in oxygen. When a splinter of wood, barely kindled in the air, is lowered into a vessel of oxygen, it bursts into flame, and smouldering charcoal, under the same circumstances, glows brightly. A bit of sulphur, burning in air with a pale blue light, flames up with greater brilliance when put into oxygen, and a piece of ignited phosphorus emits dazzling light in oxygen.

Some substances, not ordinarily classed among combustibles in air, burn readily in oxygen. A steel watch spring, for example, though heated to a red heat, cools in air as soon as the source of heat is removed, and is simply incrusted with the blacksmith's scale of burnt iron; but if we take the pains to make a little spiral of such a spring, by winding it tightly upon a glass rod and heating it in that position until the temper of the steel is so far removed that the spring remains coiled when loosened from the rod, attach to the end of the spiral a bit of wood, ignite the wood and plunge the spiral into a roomy jar of oxygen, the heat from the burning wood is sufficient to kindle the steel in the oxygen to vivid combustion, accompanied by brilliant scintillations of the scattered fragments of burning iron. A considerable portion of the metal burns, but the heat generated in the process is so intense that, before the oxygen can get at all the iron to combine with it, globules of the melted metal are loosened from the spring, and fall; so that it is a wise precaution to prevent breakage of the jar in this experiment by using, to contain the oxygen, a bottomless jar standing in water.

Oxy-hydrogen Blowpipe. Hydrogen, as we have seen, combines with pure oxygen or oxygen in air. An easy and safe way of bringing about the combination of hydrogen with oxygen is by means of the *oxyhydrogen blowpipe.* In this apparatus each gas is conveyed from the iron tank, or other reservoir containing it, through a separate pipe to the point where the two gases meet. The hydrogen is ignited first in the air, and the oxygen is then gradually turned on and admitted to the interior of the hydrogen flame, until the combustion appears to be at its greatest intensity. Naturally oxygen of the surrounding air takes part in the combustion of the hydrogen on the outside of the flame, but when the oxygen is supplied liberally, the chief part of the combustion takes place between the pure oxygen and the hydrogen. The light produced by the flame itself is very faint; but the heat is the most intense obtainable by artificial means with the exception of that of the electric arc, and when supplied to many solid substances is capable of raising them to a temperature at which they glow with great brilliance. The

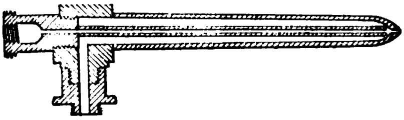

FIG. 14. — Oxyhydrogen Blowpipe.

Calcium Light. *calcium light,* so frequently employed for powerful illumination, is simply a cylinder of pressed lime heated by means of an oxyhydrogen flame to a temperature of intense incandescence. Platinum, which is useful to the chemist on account of its unchangeability when subjected to ordinary sources of heat, melts easily in the oxyhydrogen flame; and a steel file thrust into the flame burns in a dazzling shower of sparks, which perhaps exceeds in beauty the display seen in the combustion of the steel spring in an atmosphere of oxygen.

Explosion of Hydrogen and Oxygen. We found in our previous experiments that mixtures of hydrogen with oxygen and mixtures of hydrogen with air are explosive when sufficiently heated, and we noted in the case of the air mixtures that the maximum explosive effect is observed when the hydrogen and air are intermixed in the proportions of two volumes to five respectively. If we experiment similarly with hydrogen and oxygen, we may find the proportions in which mixtures of these gases are most violently explosive. By filling test-tubes with varying proportions of the gases and lighting the mixtures, we find that the maximum effect is reached when the hydrogen fills *two thirds* of the tube, and the oxygen the remainder; that is, when the gases are mixed in about the proportions of two parts of hydrogen to one of oxygen, the proportions in which these gases are evolved from water.

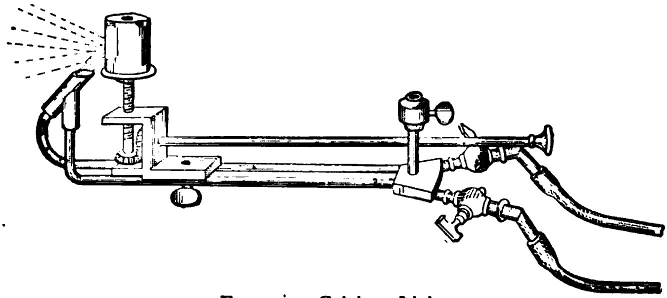

FIG. 15. — Calcium Light.

These experiments should be conducted only on a small scale, and the use of containing vessels of glass larger than an ordinary test-tube is unsafe. It is possible, however, to perform with safety the experiment of exploding a liter or two of the mixed gases, if we take the trouble to use soap bubble films as containers of the gases. A *soap solution*, **Soap Bubbles.** suitable for this purpose, may be prepared by cutting into thin shavings 125 grm. of pure castile soap, pouring on the shavings 1 liter of warm water, shaking the soap and water well together until the resulting saturated solution settles clear on standing, and then pouring off the clear solution and adding to it 125 $cm.^3$ of glycerine. A glass bell jar, open at the bottom, and fitted at the top with a stopcock and rubber outlet tube, may be utilized as a *gas holder.* Hold the jar inverted and filled with water in a large pneumatic trough, and introduce into it, first, one volume of oxygen, and then two volumes of hydrogen. Place in a large iron mortar the soap solution, submerge in it the end of the outlet tube from the gas holder, and fill the mortar with soap bubbles by opening the stopcock and rapidly lowering the gas holder in the pneumatic trough, thus forcing a current of the mixed gases into the soap solution. On bringing to the mass of bubbles, which rests upon the surface of the water, a lighted taper fixed upon a rod of such length that the experimenter may stand at a safe distance from the mortar, a violent explosion results illustrating the energy developed in the combination of hydrogen and oxygen. It is very evident why, in using an oxyhydrogen blowpipe, we lead the gases separately to the nozzle of the blowpipe so that they may combine continuously in small amounts. *It is a wise precaution, whenever experimenting with considerable amounts of both hydrogen and oxygen, to guard against accidents from their intermixture by drawing off and testing separately small portions of the gases before heating them or acting upon them chemically.*

Products of Combustion. Now let us give attention to the products formed by the combustion of the various elementary substances which we have burned either in air or in oxygen. These products prove, upon investigation, to be compounds of the individual elements with oxygen, and they are called *oxides.*

When hydrogen burns in air or in oxygen we know that it combines with the oxygen to form water, or hydrogen oxide, a compound of hydrogen and oxygen.

$$\text{Hydrogen} + \text{Oxygen} = \text{Hydrogen Oxide}$$

Similarly, when charcoal, which is nearly pure elementary carbon, burns, a compound of carbon with oxygen is formed which we call carbon dioxide. The product is the same, whether the combination is effected in air or in pure oxygen, though its formation is much more rapid in oxygen, as is made evident by the increased intensity with which the charcoal burning in air glows when placed in pure oxygen.

$$\text{Carbon} + \text{Oxygen} = \text{Carbon Dioxide}$$

Carbon dioxide is gaseous and invisible, and has no odor; but its presence in the vessel in which the combustion of the charcoal in air or in pure oxygen has occurred may be recognized by means of some suitable chemical test. Thus, carbon dioxide is known to produce a milky emulsion with limewater, while no such effect is produced by oxygen or by a few cubic centimeters of ordinary air. If, therefore, we shake a little clear limewater in the tube in which the charcoal has just been burned, the production of milkiness in the limewater may be taken to indicate, under these particular circumstances, the presence in the flask of carbon dioxide.

So also, when sulphur burns, either in air or oxygen, we note the pungent odor characteristic of the gaseous compound of sulphur and oxygen, which is sulphur dioxide.

Sulphur + Oxygen = Sulphur Dioxide

The odor is, in this instance, a sufficient indication of the presence of the oxide formed. When phosphorus burns in an abundant supply of oxygen, the floating white cloud of finely divided solid matter is a compound of phosphorus and oxygen, which bears the name phosphorus pentoxide.

Phosphorus + Oxygen = Phosphorus Pentoxide

The production of a dark-colored iron oxide may be observed during the combustion of a steel spring in an atmosphere of oxygen, or when a file is burned in the oxyhydrogen flame.

Iron + Oxygen = Iron Oxide

Oxides. The oxides we have studied, *e.g.* mercury oxide, hydrogen oxide, carbon dioxide, sulphur dioxide, phosphorus pentoxide, and iron oxide, as well as the magnesium oxide and copper oxide of earlier experiments, are typical of an immense number of oxides, solid, liquid, or gaseous, which occur naturally in greater or less quantities or may be produced by direct union of the elements, or, as we shall see in the course of our work, by the indirect method of decomposing more complex compounds until oxides are left as products. Every element, with the exception of fluorine, bromine, and the newly discovered inert elements, is capable of forming an oxide. Among the oxides, we find some which are gaseous under ordinary conditions, like carbon dioxide and sulphur dioxide; oxides which are liquid, like hydrogen oxide; and oxides which are solid, like phosphorus pentoxide, copper oxide, and iron oxide. So also we have oxides soluble in water, like the solid phosphorus pentoxide, and the gaseous carbon dioxide; and oxides practically insoluble in water, like the solid copper oxide; and between these limits we find representatives of various degrees of solubility. We have oxides of every color and of many degrees of heaviness. Moreover, the state and properties of oxides may be more or less changeable with variations in external conditions. For example, we know hydrogen oxide as a gas, a liquid, a solid, according as conditions of temperature and pressure vary; while magnesium oxide is solid at all temperatures within the range of ordinary experimentation.

Oxides and Oxidation. We find, therefore, in considering the oxides, that some may be formed by direct combination of an element with oxygen, and some are not so formed directly; some are gaseous, some liquid, some solid at ordinary temperatures, and some capable of existing in more than one of these states; some soluble in water, and some insoluble. In general, *the combustion of elementary substances in oxygen or in air produces compounds of these substances with oxygen, termed oxides, and the process by which such compounds are formed is known as oxidation.* The combustion of compound substances in oxygen is also a process of oxidation and may result in the production of oxides; but the products of combustion of a compound may often contain several elements and be more complex than the compounds of the individual component elements with oxygen which we call oxides.

The simplest way to effect oxidation is to heat in air or oxygen the substance to be oxidized, as may be done in the case of mercury, and with hydrogen, carbon, sulphur, phosphorus, and iron. Many substances, however, are more readily oxidized, or, indeed, may only be oxidized by acting upon them chemically with a second substance which contains oxygen so loosely combined as to be given off readily, in the course of a chemical change, to the substance to be oxidized. *Such a compound, which readily gives up its oxygen to other substances, is termed an oxidizer.*

Reduction and Reducers. *The reverse process to oxidation,* i.e. *the removal of oxygen from an oxide, or other compound containing oxygen, is known as reduction.* The simplest reduction is effected by merely heating the oxygen compound at such a temperature and under such conditions that the oxygen is driven off, as was the case in our experiments with mercury oxide and with the oxygen compound, potassium chlorate. Many oxygen compounds are more readily reduced, or in some instances may only be reduced, by heating them or otherwise inducing them to act chemically with a second substance, which may or may not already contain oxygen, but which possesses a strong attraction for the oxygen of other substances, and which may, therefore, be used to assist in removing oxygen from the substance to be reduced.

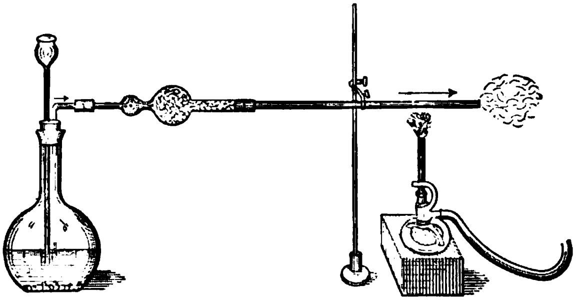

FIG. 16. — Passing Hydrogen over Heated Copper Oxide.

Such a substance, either element or compound, which readily removes and combines with oxygen from other substances, thereby becoming itself oxidized, is termed a reducer.

Reduction of Copper Oxide with Hydrogen.

The reduction of copper oxide to copper and the subsequent reoxidation of the copper to copper oxide may readily be made the subject of an experiment. Copper oxide is not reduced by mere heating with ordinary sources of heat, and we therefore look for some efficient reducer with which to remove oxygen from its close combination with the copper. Of the substances which we have found to combine with oxygen, we should naturally select for the purpose of reducing copper oxide one which shows a disposition to combine with free oxygen easily, and to hold it firmly; furthermore, the substance which we choose as a reducer must be incapable of entering itself into combination with copper under the conditions of the experiment. Such a substance is hydrogen, which, as we have seen, combines with oxygen with great energy, producing a volatile oxide of great stability, and which, as proves to be the case, does not itself form any compound with copper under the conditions of the experiment.

Let us introduce some copper oxide into a hard glass tube drawn out at one end to a jet, connecting the larger end of the tube with a calcium chloride drying tube, which in turn is joined to the delivery tube of a hydrogen generator. Heat the tube beneath the copper oxide while a slow current of hydrogen passes. The copper oxide gives its oxygen to the hydrogen rapidly, turning from black to red, and often glowing with the heat evolved, while the water formed by the union of the hydrogen and oxygen collects in the cooler end of the tube or escapes in the form of steam. The metallic copper left in the tube in finely divided condition may, after cooling, be identified by removing a portion and burnishing it with a knife blade to bring out the luster and color of the polished metal. *When copper oxide is heated strongly in hydrogen, the hydrogen withdraws the oxygen from the oxide, hydrogen oxide escapes, and copper remains.* The reduction of copper oxide has been effected by the oxidation of the hydrogen, whence it appears that the hydrogen acted as a reducer to the copper oxide, and the copper oxide served as an oxidizer for the hydrogen.

Copper Oxide + Hydrogen = Hydrogen Oxide + Copper

To effect the reoxidation of the copper, it is sufficient to heat the copper in a brisk current of oxygen or air. Let us remove from the combustion tube, containing the reduced copper, the hydrogen generator and drying tube. Connect one end of the combustion tube with a glass tube reaching nearly to the bottom of a tightly stoppered washing flask containing water; arrange a second tube leading out of the flask, and connect it with an aspirator. Draw a current of air through the combustion tube, regulating its speed by observing the rapidity of the passage of bubbles through the water, meanwhile heating the combus-

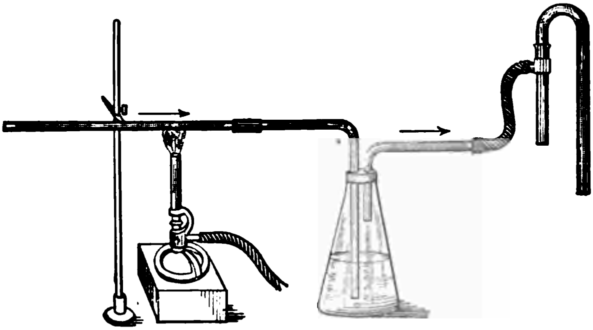

FIG. 17. — Passing Air over Heated Copper.

tion tube until the uniform dark color of the contents indicates the complete reconversion of the copper into copper oxide. This experiment is in principle precisely like that earlier experiment, in which, by heating in a crucible a weighed amount of copper exposed to air, we converted copper to copper oxide, and noted the weights of each of these substances involved in that process, as indicated by the equation:

Copper + Oxygen = Copper Oxide

Reduction of Iron Oxide with Hydrogen.

An experiment exactly similar in every detail may be made with iron oxide to show how hydrogen may reduce it with the formation of water. The black residue, consisting of iron, or of an oxide of iron containing a very small amount of oxygen, may, because of its extremely fine division and the large surface which its particles consequently present to the air, frequently be made to ignite spontaneously and to burn brightly by simply pouring it out slowly, while still hot, into an open dish. At all events, the reoxidation of the residue may be readily effected by gently heating it in a crucible open to the air.

Carbon as a Reducer.

Carbon is another reducing agent, very valuable on account of its cheapness and efficiency in operations in which oxides are to be reduced to metals. We may imitate such process by mixing copper oxide with about one eighth of its weight of carbon, in the form of finely divided charcoal, and heating the mixture to redness in a glass tube. The copper oxide is reduced to copper. *When copper oxide and carbon are heated strongly together, the carbon withdraws the oxygen from the copper oxide, an oxide of carbon escapes into the air, and copper remains.*

Copper Oxide + Carbon = Carbon Dioxide + Copper

The case is quite similar to that of the copper oxide and hydrogen. The reduction of the copper oxide is accompanied this time by the oxidation of the carbon. The carbon acts as a reducer to the copper oxide, the copper oxide, on the other hand, serving as an oxidizer of the carbon.

Oxidation and Reduction.

The terms *oxidation* and *reduction*, as we have employed them, are exactly antithetical and their meaning is unmistakable. Sometimes, however, the word *oxidation* is applied to certain chemical changes of combination in which oxygen does not figure directly as a factor, but in which compounds having relation to oxides are formed, while the word *reduction* is extended to apply broadly to the simplification of any compound by the removal from it of an element or elements, without regard to whether the substance so removed is oxygen or something else, or whether the substance effecting such removal has the power to combine with oxygen. So also the word *combustion*, which as ordinarily employed refers only to such processes of oxidation as are accompanied by the evolution of heat and light, is also applied broadly to include similar energetic combination of substances with substances other than oxygen. The general subject of combustion or burning was very early made the object of investigation, but because of a lack of quantitative methods of study, the part which gases play in such chemical changes was not understood, and for many years the conclusions reached were erroneous. The discovery of oxygen by Scheele and by Priestley, the investigation of carbon dioxide by Black and of hydrogen by Cavendish, and the later quantitative studies of the chemical changes which these substances enter, led directly to the acceptance of the true explanation of what we know as the phenomena of oxidation, first proposed, in 1786, by Lavoisier. These achievements marked the beginning of modern scientific chemistry.

Combustion.

CHAPTER V

WATER

In the experiments in which we decomposed water, or in other words made an analysis of water, by the agency of the electric current, we noted that the gaseous products, hydrogen and oxygen, were, so far as we then observed, the sole products of the decomposition, and that the volume of the hydrogen evolved proved to be about twice that of the oxygen. We have also recognized the product of hydrogen burned in oxygen or in air as water. It remains now to study the synthesis of water quantitatively, under conditions such that we may determine with accuracy the proportion in which pure hydrogen and pure oxygen combine to form water.

Volumetric Synthesis of Liquid Water.

We have found that hydrogen and oxygen which may be evolved from water by an electric current may be easily combined by an electric spark of high tension. The mixed gases may be contained to best advantage in a stout graduated *eudiometer*, the upper end of which is closed, while the lower end is effectively sealed by immersion in mercury contained in a shallow vessel. The spark is sent through the mixed gases between the small platinum wires, which have been fused into the glass near the closed end of the tube, in such a manner that the inner terminals will be near and opposite to one another, although not in contact, while the outer ends of the wire may be readily connected in the secondary circuit of a small induction coil. While the mercury does not tend to dissolve either gas, and will not combine chemically with either gas at ordinary temperature, it is nevertheless necessary to use considerably more hydrogen than will combine with the oxygen present, in order to prevent the combination of some of the oxygen with mercury at the high temperature that is produced locally by the ignition of the two gases. However, since we may know exactly how much hydrogen and how much oxygen we start with, and how much hydrogen is left over at the end, we may readily determine how much hydrogen has combined with the known amount of oxygen taken.

Let us then, for this experiment, provide ourselves with a eudiometer, a shallow dish containing mercury, a tall, narrow cylinder nearly filled with mercury, an electric battery, and a small induction coil for generating a secondary current of high tension to make the spark. The eudiometer is filled completely with clean, dry mercury and inverted in the mercury cylinder, so that its mouth dips only slightly beneath the surface of the mercury. The glass delivery tube of a hydrogen generator is now dipped in the mercury and brought under the mouth of the eudiometer tube, and pure hydrogen is introduced until the tube is about half filled. The tube is now adjusted in the cylinder until the level of the mercury is the same in both the tube and the cylinder, and the fixed and definite volume of hydrogen, confined in the tube under the pressure of the outside air and at the prevailing atmospheric temperature, is read accurately. Pure oxygen is now similarly introduced into the tube from a reservoir, to an amount not exceeding one eighth of the volume of the hydrogen, the level of the mercury in the tube is again adjusted to that of the mercury in the cylinder, so as to bring the mixed gases under atmospheric pressure, and the volume of the mixed hydrogen and oxygen, in which the hydrogen is present in excess, is read accurately.

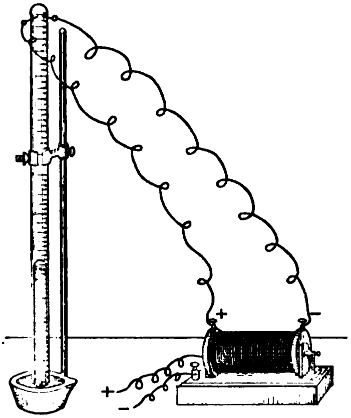

FIG. 18. — Explosion of Measured Volumes of Hydrogen and Oxygen in a Eudiometer.

The tube containing the hydrogen, oxygen, and mercury is transferred carefully, and without admission of air, to the shallow dish containing mercury, and clamped firmly, so that the explosion to follow may not move it, with its mouth resting upon a rubber pad submerged beneath the mercury. A spark is passed between the platinum electrodes, by momentarily closing the secondary circuit of the induction coil, there is a flash of light in the tube, and the oxygen and an equivalent volume of hydrogen combine to form a few drops of moisture, the volume of which is insignificant, a partial vacuum being formed in the tube, into which the mercury will freely rise, when we slide the tube laterally off the rubber pad. The gas finally remaining in the tube is evidently the residual hydrogen, and its volume is read accurately at the pressure and temperature of the atmosphere, and subtracted from the original volume of hydrogen to indicate what volume of hydrogen disappeared in combining with oxygen. The volume of oxygen which combined with the volume of hydrogen is equal to the difference between the volume of the mixed gases and the volume of the original hydrogen.

Let us suppose, for example, that our experiment gives us these results:

Volume of hydrogen introduced . . .	40 cm.^{3}
Combined volume of hydrogen and oxygen .	45 cm.^{3}
Volume of residual hydrogen after the explosion	30 cm.^{3}

By subtracting the first quantity from the second we have:

Volume of oxygen used	5 cm.^{3}

By subtracting the last quantity from the first we have:

Volume of hydrogen used	10 cm.^{3}

It is easy to see that 10 cm.^{3} of hydrogen were used up in combining with 5 cm.^{3} of oxygen, or, in other words, that in the volumetric synthesis of water within the limits of accuracy of an experiment, two volumes of hydrogen combine with one volume of oxygen, a result in accord with that obtained in the volumetric analysis of water. We purposely made our experiment quite simple, giving little attention to details, but when the experiment is performed with every precaution to insure exactness, it has been found that the proportions in which hydrogen and oxygen combine vary from the ratio at 2 : 1 by an amount equal to about 0.001 of the whole volume. *The recent and very exact work of Morley places the ratio by volume in which hydrogen and oxygen combine to form water as 2.0027 : 1.* For general purposes we may consider that the result of our experiment was sufficiently near the truth, and say that *approximately two volumes of hydrogen combine with one volume of oxygen in the production of water.* The volumetric synthesis of water was first performed in 1781 by Cavendish, was repeated by Gay-Lussac and Humboldt in 1805, and has been subsequently studied with great care by many investigators.

Volumetric Synthesis of Gaseous Water.

It is interesting to know what volume the water formed by the union of two volumes of hydrogen with one volume of oxygen will occupy if it be kept in the state of vapor. Let us repeat our synthesis with such modifications as are necessary to keep the water produced in the form of vapor, at a definite temperature, so that its volume, together with that of the uncombined hydrogen, may be readily measured. We will employ a eudiometer tube like that of the former experiment, observing the precautions to inclose it from the upper extremity, where the platinum electrodes are situated, down throughout a sufficient part of its length, with a glass cylinder or "jacket," into the top of which steam is injected from a flask or other vessel utilized as a boiler, and from the bottom of which water and uncondensed steam may escape. Let us fill the tube, thus jacketed, with clean, dry mercury, invert it as in the previous experiment in a cylinder containing mercury, and introduce hydrogen and oxygen to a volume not exceeding one eighth that of the hydrogen. We will take care, however, to measure each gas individually at the temperature of the steam, which should be introduced into the jacket before the measurements are made. This may be accomplished by noting the height of the mercury in the tube above that in the cylinder at the time of the first measurement of the mixed gases, and carefully adjusting the mercury to the same level before measuring the residual hydrogen. The electric spark is passed, the tube is lowered until the level of the mercury in it stands at the original height above the level in the cylinder, and the volume of the residual gas, consisting of the water vapor formed and the excess of hydrogen, is measured. The level of the mercury in the tube being above that of

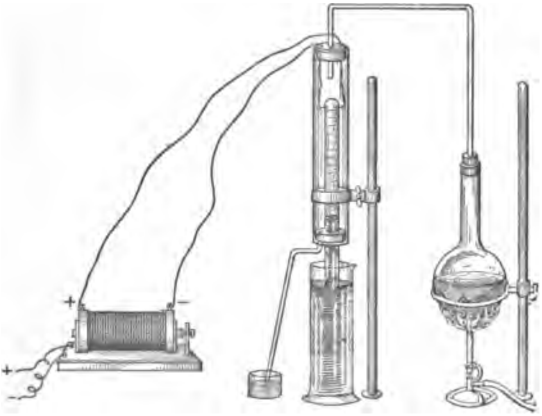

FIG. 19.— Explosion of Measured Volumes of Hydrogen and Oxygen in a Eudiometer surrounded by a Steam Jacket.

the mercury in the cylinder, the residual gases are of course under a pressure less than one atmosphere by an amount represented by this difference in levels, and so the steam in the jacket, itself at atmospheric pressure, is sufficiently hot to keep the water formed by the explosion in a state of vapor under the diminished pressure of the gas in the tube.

Let us suppose that our second experiment gives us:

Volume of hydrogen introduced . . .	40 cm.^{3}
Combined volume of hydrogen and oxygen .	45 cm.^{3}
Combined volume of water vapor and residual hydrogen after the explosion . . .	40 cm.^{3}

By subtracting the first quantity from the second we have:

Volume of oxygen used	5 cm.^{3}

An inspection of the last two quantities, however, reveals the surprising fact that the 5 cm.^{3} of oxygen, in combining with a quantity of hydrogen, forms a volume of water and residual hydrogen equal to the volume of the original hydrogen. We have previously found this volume of hydrogen to be 10 cm.^{3}, so it becomes plain that 10 cm.^{3} of hydrogen were used up in combining with 5 cm.^{3} of oxygen to form 10 cm.^{3} of water vapor; or, in other words, *approximately two volumes of hydrogen combine with one volume of oxygen to form two volumes of water vapor.* This relationship of volume between the water vapor and the hydrogen and oxygen was first determined by Gay-Lussac.

Having found that one volume of oxygen combines with very nearly two volumes of hydrogen to form water, and that any given volume of oxygen weighs 15.90 times as much as the equal volume of hydrogen, it follows that 15.90 parts by weight of oxygen combine with very nearly two parts by weight of hydrogen to form very nearly 17.90 parts by weight of water vapor.

Gravimetric Synthesis of Water.

We may determine more accurately the definite proportions by weight in which hydrogen and oxygen combine by a direct gravimetric synthesis of water with materials weighed, not measured. We must select for our purpose some substance, suitable for weighing, which does not easily change spontaneously or in the presence of air or water, but which will nevertheless react readily with hydrogen to form a stable product which may be weighed accurately.

The black copper oxide, which we have found to be easily reduced to metallic copper by hydrogen, fulfills these conditions excellently. We have only to weigh out a suitable amount of copper oxide, pass a weighed amount of dry hydrogen over it at high temperature until the oxide is completely reduced, and condense and weigh the water produced.

Provide a flask, fitted with a stopcock, and fill it with pure, dry hydrogen under a pressure considerably greater than that of the atmosphere, and weigh the flask with its contents. Fill a combustion tube of hard glass with copper oxide, and weigh tube and contents, and similarly prepare and weigh a U-shaped absorption tube, filled with calcium chloride, which, as we know, has great capacity for absorbing water. Allow the hydrogen to flow slowly from the flask over the hot copper oxide, while the water which is produced is driven forward for the most part and collected in the absorption tube, which is protected against outside moisture by a drying tube and bulbs. When the hydrogen no longer flows from the flask, shut the stopcock, close the end of the absorption tube, allow the combustion tube to cool, and disconnect the flask and weigh it. Draw a current of dry air, by means of an aspirator, through the cool combustion tube and absorption tube, until all traces of moisture remaining in the former have been transferred to the latter, and then weigh each of these tubes separately. The loss of weight of the flask represents the hydrogen burned; the loss of weight of the combustion tube measures the oxygen used in burning the hydrogen; and the increase in weight of the absorption tube represents the water formed in the combustion of the now known amounts of oxygen and hydrogen. When the experiment is most carefully made, it is found that

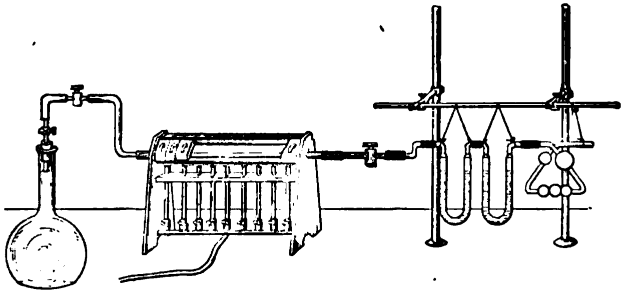

FIG. 20. — Passing Hydrogen over Heated Copper Oxide under Quantitative Conditions.

Equivalents of Hydrogen and Water. *88.82 parts by weight of oxygen combine with 11.18 parts by weight of hydrogen to form 100 parts by weight of water; or expressing the ratios more simply in terms of oxygen taken as 16, 16 parts by weight of oxygen combine with 2.015 parts by weight of hydrogen to form 18.015 parts by weight of water.* By the gravimetric synthesis of water we have found the equivalents of hydrogen and of water to be 2.015 and 18.015 respectively.

Equivalent of Magnesium. Having thus determined the equivalent weight of hydrogen, it is possible to include in our series the equivalent weights of those elements which are capable of replacing hydrogen in compounds. We have found experimentally that 1 part by weight of magnesium replaces 0.0827 parts by weight of hydrogen when magnesium acts upon sulphuric acid. *Since the equivalent of hydrogen is* 2.015, *the equivalent of magnesium found from the proportion* $0.0827 : 1 = 2.015 : x$, *proves to be 24.36.* Similarly, since, as we have seen, 1 part by weight of zinc replaces 0.0308 parts by weight of hydrogen from sulphuric acid, the *equivalent of zinc* proves to be

$$\frac{2.015}{0.0308} = 65.4$$

Water. Water, as every one knows, occurs abundantly in the free state, and, as we shall soon see, in combination with other things. In the ocean it covers four fifths of the earth's surface. From the ocean, water is evaporated by the sun's heat, is held in the air as invisible moisture, condensed as clouds, precipitated as dew or rain, or as frost, snow, or hail, and finally returned to the ocean through the agency of springs and streams carrying into it various matters in solution. Pure water is tasteless, odorless, and in small amount is nearly colorless, though when viewed in mass, as in glaciers and clear lakes, water is seen to possess a distinctly blue color. We recognize water in the free state in three conditions or *phases*, — solid ice, liquid water, and gaseous steam, — which, though possessed of similar capacities to react chemically with other substances, are characterized individually by certain physical properties.

Specific Gravity and Specific Volume. Of such properties the density or concentration of mass is one of the most important as well as one of the most obvious. *As a measure of concentration of mass, we find it convenient to take the specific gravity of the substance, or the* *weight of the unit volume of the substance in terms of the weight of the unit volume of some standard substance.* The concentration of mass is proportional to the specific gravity and is inversely proportional to the *specific volume* of the substance, or that volume which is occupied by the unit weight of the substance in terms of the volume occupied by the unit weight of the standard substance.

The weight of 1 cm.^{3} of water at 4° is almost exactly 1 grm., and so it is frequently convenient to take water at 4° as a standard substance with which to compare concentrations. *The weight in grams of 1 cm.^{3} of a substance, or its specific gravity referred to water at 4°, expresses directly the concentration of the substance as compared with water at 4°. The volume in cubic centimeters occupied by 1 gram of a substance, or its specific volume, referred to water at 4° (obviously the reciprocal of the specific gravity), expresses inversely the concentration of the substance as compared with water at 4°.*

In the following table are given certain experimental data relating to the specific gravity and the specific volume of water:

SPECIFIC GRAVITY AND SPECIFIC VOLUME OF WATER

PRESSURE (mm.)	TEMPERATURE (°)	SPECIFIC GRAVITY (Water at 4° = 1)	SPECIFIC VOLUME (Water at 4° = 1)	PHASE
760	0	0.9173	1.0901	Solid
760	0	0.99987	1.00013	Liquid
760	4	1.00000	1.00000	
760	10	0.99973	1.00027	
760	20	0.98823	1.00177	
760	50	0.98813	1.01200	
760	100	0.95863	1.04327	
760	100	0.00059	1696.	Gas
(195.5 × 760)	370	0.429	2.33	Critical Condition

Physical Properties of Water. In these data several interesting facts come to light. The change of a body from the solid to the liquid phase is ordinarily accompanied by an increase in the volume of that body, but to this rule the behavior of water furnishes an exception.

Ice melts under ordinary atmospheric conditions of pressure at a temperature so definite that this is taken as the zero of the centigrade scale. Great changes in pressure affect, however, the melting point of ice, which under a pressure of 1000 atmospheres falls as low as — 7°. When ice melts to water at the same temperature, it decreases in volume, and conversely when water freezes it increases in volume. The change of volume is less than a tenth of the entire volume of the water; but the expansive force of freezing water is so tremendous that a cast-iron shell filled with water and tightly plugged may be burst by lowering the temperature to the freezing point, and the process of alternate melting and freezing of water in cracks and crevices is powerfully effective in rock disintegration, and in the natural formation of soils from rocks.

Ordinarily, when a liquid is heated gradually above the temperature at which it ceases to exist in the solid form, its volume is regularly increased, but here is another instance in which the behavior of water is exceptional. *As the temperature of water rises from 0° the volume at first decreases, and afterwards increases. The greatest decrease of volume, and therefore the densest condition of water, is found at 4°.* This apparently simple though abnormal fact of the irregular change of volume of water with changing temperature is of the greatest importance in its effect upon the climate of those regions of the earth in which the winter temperature produces ice. For, as the water in the lakes and rivers grows colder than 4°, its slightest expansion lessens its specific gravity, or, in other words, causes any given volume of it to become lighter than the same volume of water that has not been so cooled. The cooler water, therefore, rises and tends to stay at the surface, so that when the freezing temperature is reached, it is at the top and not at the bottom that the ice forms, and when the ice is once formed, its specific gravity keeps it at the surface to serve as a protecting coat to the water below against the atmospheric cold. So it happens that the cold of winter does not freeze lakes and rivers from the bottom upward, and the heat of summer is not expended to such an extent in thawing the ice of winter as would be the case if the contraction of water with falling temperatures were regular. Above 4° the volume of water increases regularly so long as it remains in the liquid phase, and here also, though the degree of expansion is not large, its force is tremendous.

Tension of Water Vapor.

When passing to the vapor phase, water expands enormously, 1 grm. of water, which at 4° occupies 1 $cm.^3$, and at 100° 1.04 $cm.^3$, filling as vapor 1696 $cm.^3$ at 100° and under normal atmospheric pressure (760 mm. at sea level, in latitude 45°). The tendency of water, solid or liquid, to expand in vaporizing is known as the *tension of water vapor*, and this tension may be measured by introducing a little water into the vacuum of a barometer and noting the resulting depression of the mercury column as compared with the height of the mercury in the ordinary barometer in which there is no water. At ordinary temperatures the depression of the mercury column covered by water is marked; and the depression is perceptible even at so low a temperature as 20° below the freezing point of water. When the temperature reaches 100°, the ordinary barometer showing a normal atmospheric pressure, the level of the mercury column in the barometer containing enough water sinks to that of the trough, showing that the pressure of the steam, or the tension of water vapor, equals that of the surrounding atmosphere. The tendency of water to vaporize is, however, conditioned by the external pressure acting against the tension of water vapor, so that the change of water from the solid phase or liquid phase is governed by the pressure exerted upon it as well as by the temperature. When water heated in an open vessel boils, it is because vaporization takes place so rapidly that the surface of the liquid is thrown into agitation, and so it is obvious that the boiling point of water, as we ordinarily observe it, is dependent upon the atmospheric pressure, which varies with the altitude of the locality and the existing meteorological conditions. This is why we are careful to state that *100° is the boiling temperature of water under normal barometric pressure of 760 mm. at the sea level, latitude 45°*. It is a matter of common experience that on the tops of high mountains water boils at a temperature appreciably below 100°. In general, increase of temperature favors the vaporization of water, while increase of pressure not only opposes the tendency to vaporize, but tends to condense the vapor to the liquid or solid phase. At a pressure of 195.5 atmospheres (195.5 × 760 mm.), and a temperature of 370°, a peculiar condition is reached at which 1 grm. of water

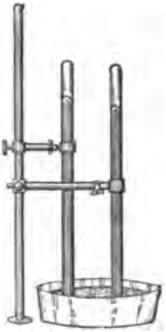

FIG. 21. — Depression of Mercury Column by Water Vapor.

occupies a volume of 2.33 cm.^{3} while neither distinctly gaseous nor distinctly liquid. Under these conditions the properties of gaseous water and liquid water become identical.

If the temperature is now lowered below 370°, the pressure remaining the same, the water is liquefied; if the pressure is increased above 195.5 atmospheres while the temperature is unchanged, the water is likewise liquefied; but above 370° no amount of pressure can liquefy gaseous water.

Critical Pressure: Critical Temperature.

The temperature above which a gaseous substance cannot be liquefied by pressure is known as the *critical temperature* or the *absolute boiling point* of the substance; the pressure which will just liquefy the gas at the critical temperature is known as the *critical pressure;* and the volume of one gram of the substance at the critical conditions of temperature and pressure is the *critical volume.* For water the critical temperature or absolute boiling point is 370°, the critical pressure is 195.5 atmospheres, and the critical volume is 2.33 cm.^{3}

The following table shows for a few temperatures the tension of water vapor expressed in barometric heights of mercury at the sea level in latitude 45°.

TENSION OF WATER VAPOR

TEMPERATURE	TENSION
— 20°	0.93 mm.
— 10	2.15
0	4.6
+ 10	9.1
+ 20	17.4
+ 40	54.9
+ 60	148.9
+ 80	355.4
+ 100	760.0

Phases of Water.

The relations which exist between temperature, pressure, and the change of phase of water may be shown by diagrammatic representation. If we represent pressures by a series of parallel horizontal lines and temperatures by a series of parallel vertical lines, every point of the diagram will mark a certain pressure and a certain temperature, and the conditions of pressure and temperature under which each phase of water may exist will be indicated by an area comprising the points indicative of certain pressures and temperatures. In the accompanying diagram, upon a small scale, exact quantitative representation is sacrificed to qualitative expression of such relations.

Every point within the area *BPC* will indicate a pressure and a temperature at which solid water may exist; every point within the area *APB* will indicate a pressure and a temperature at which water may be liquid; while every point within the area *APC* will show a pressure and a temperature at which water exists as gas or vapor. Every point in the curve *PA* shows a pressure and a temperature at which liquid water and water vapor may exist together, every point in the curve *PB* represents a pressure and a temperature at which liquid and solid water may exist together, while every point in the curve *PC* represents a pressure and a temperature at which solid water and water vapor may exist together. The point *P* in which the three curves meet is called the *triple point* and indicates the one condition of temperature (nearly 0°) and pressure (4 mm.) at which all three phases of water may coexist. The point *A*, at the end of the curve made up of points which show the temperatures and pressures at which liquid water and water vapor may coexist, will indicate the critical pressure and the critical temperature; while the continuation of the curve *AP* into the solid territory indicates conditions of pressure and temperature under which water may be cooled below 0° without freezing, as sometimes happens with pure water kept perfectly still. The fact that water may be thus supercooled is the reason why we take the melting point of ice, which is definite at definite pressures, as a physical constant rather than the freezing point of water.

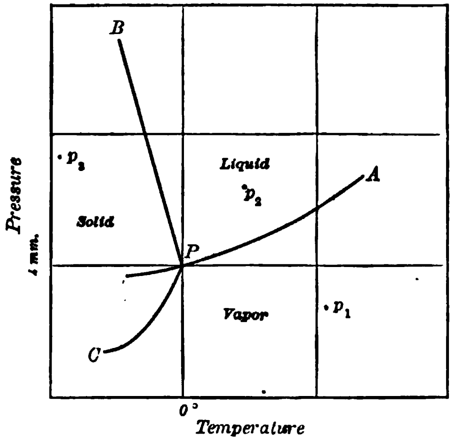

FIG. 22. — Diagram representing Phases of Water.

Specific Heat. When heat is applied to a substance without causing change of phase the temperature of the substance rises. Of all known substances, liquid water has the greatest capacity for heat for a given rise in temperature, and so the heat capacity of liquid water serves conveniently as a standard of the heat capacities of other substances; but since the heat capacity of water changes slightly with the temperature, it is customary for ordinary purposes to refer heat capacities to that of water at 18°, the average atmospheric temperature. *The quantity of heat required to raise by 1° the temperature of 1 grm. of water at 18° is a convenient unit of heat capacities, or specific heats, and we call it a common calorie.*

Latent Heat. When a change of phase occurs in consequence of the application of heat to water, a very remarkable disappearance of heat accompanies the change of phase. When heat is applied to ice, with care to keep the ice and the water formed thoroughly stirred, the temperature of the liquid remains at zero until all the ice has melted. Evidently heat vanishes in the melting of ice at 0° to water at the same temperature. Conversely, it is a fact which may be shown experimentally under suitable conditions that the freezing of water is accompanied by the liberation of exactly the same amount of heat that will be required to again melt the ice which is formed. *The heat which disappears when ice is melted and reappears when the water freezes is known as the latent heat of water, or the latent heat of fusion of ice.* The heat required to melt 1 grm. of ice at 0° is susceptible of accurate measurement, and proves to be 79 times as much as the heat required to raise by one degree the temperature of 1 grm. of water taken at 18°, — or 79 common calories.

As liquid water at 0° is heated under definite pressure, the temperature rises regularly until the boiling point, 100° if the atmospheric pressure is normal, is reached, and thereafter remains unchanged until the water is entirely vaporized to steam at the same temperature. *Heat disappears in converting water to steam at the same temperature, and in condensing the vapor to liquid this heat reappears.* Here again we are dealing with latent heat, but this time it is the *latent heat of steam or water vapor, or the latent heat of vaporization of water.* Like the latent heat of fusion of ice, it is susceptible of accurate measurement, and it is found that the heat required to vaporize 1 grm. of water at 100° is 536 common calories.

Climate. That the latent heat of water and of water vapor often has important effects upon climate and upon the agricultural resources of a country is plain when we remember that the shores of inland lakes or arms of the sea in northern latitudes are warmed in winter by the liberation of enormous quantities of heat latent in the water and set free when the ice is formed, with the consequence that lands so situated are correspondingly cooled in the spring by the removal of the heat necessary to again melt the ice; and that seaboard countries are continually cooled by the evaporation of the water, while the heat is carried latent to the upper regions of the atmosphere, to be again liberated by the condensation of moisture into rain.

Many other specific properties of water are likewise of interest. The relations of water to other substances are of great importance and will be considered when we get on a little farther.

CHAPTER VI

WATER SOLUTION, HYDRATION, AND HYDROLYSIS

Solvents and Solutes. WATER acts as a *solvent* of many substances, solid, liquid, and gaseous, which may be termed *solutes*, but the degree of the solvent effect of the water varies with the individual characteristics of the solutes or substances acted upon. Some solids, like salt and sugar, dissolve easily in water, while other solids, like sand and glass, are so slightly soluble that they are ordinarily considered to be insoluble. Some liquids, like alcohol and glycerine, dissolve freely in water, as we see when we shake a few cubic centimeters of these substances with water; other liquids, like chloroform and ether appear, when treated similarly, to dissolve only slightly in water; while some liquids, like ordinary oil, which is incapable of mixing with water, do not dissolve at all. That water ordinarily contains gas in solution may be shown easily by inverting a test-tube filled with water in a pneumatic trough and heating the tube until bubbles of gaseous matter rise and gather above the water, and we shall learn later that the sparkling quality of ordinary soda water is due to gaseous carbon dioxide dissolved in the water. *It is plain, therefore, that the solvent power of water varies with the substances which we attempt to dissolve*, and not only is this so, but if we extend our experimentation, it becomes evident that *temperature often has much to do with the degree of solubility of the substance attacked.*

Solvent Power of Water for Substances. We may study the solvent effect of water for solid, liquid, and gaseous bodies by experimenting with a few substances whose behavior with water is fairly typical. In order to observe the conditions effecting the solution of solid bodies, let us first put 5 grm. of potassium dichromate into 5 cm.^{3} of water, and boil, supplying the water as it evaporates, until the substance dissolves. The solution thus formed will, upon cooling, throw out a portion of the potassium dichromate in crystals, while a part still remains in solution, as is shown by the color of the clear liquid above the crystals.

Crystals. We may note incidentally that *crystals* are solids bounded by plane surfaces or *faces*, and if we pursue our study of crystals, we come to know that crystal faces are arranged symmetrically, and that crystals are possessed of properties varying in degree with the directions followed within them and dependent upon the type of symmetry of the crystals, which are classed accordingly in six different classes or systems — viz.: (I) the *isometric system*, (II) the *tetragonal system*, (III) the *hexagonal system*, (IV) the *orthorhombic system*, (V) the *monoclinic system*, (VI) the *triclinic system*.

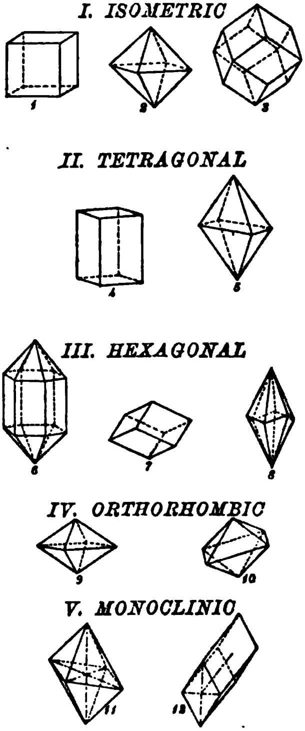

FIG. 23.— Crystal Forms.

Effect of Heat on Solution. Evidently the solvent power of water for potassium dichromate increases as the temperature rises, and decreases as the temperature falls. On the other hand, if we put 5 grm. of common salt in 5 $cm.^3$ of water, boil, filter out by means of a dry filter the excess of undissolved salt, very little salt is precipitated from the solution on cooling, showing that the solubility of salt in water is not notably changed by a change in the temperature of the mixture. Again, if we make of calcium oxide, or "lime," a cold *saturated solution*, — a solution in which under the conditions the greatest possible amount of solute is present, — and if we heat this solution to the boiling point, an incrustation of lime is deposited on the walls of the test-tube in which the heating takes place, thus showing that the lime is held in solution more easily by cold water than by hot water, and that the solvent power of water for lime is decreased by a rise in the temperature of the mixture. We may say, in general, that *while the application of heat to a mixture of a solid substance and water usually increases the solvent effect of water for that substance, it may in some* *cases be without effect, or may even decrease the solubility of a substance in water.*

Liquids, like alcohol and water, which are freely soluble in one another at the ordinary temperature, are generally found to be freely miscible in any proportions at all temperatures. *Changes of temperature in general influence the solubility in water of liquids far less than they affect the solubility of solids.*

Henry's Law. If we take a solution of a gas in water, as for instance the solution of carbon dioxide, ordinarily known as "soda water," we find that the solution, which was formed by forcing the gas into the water under high pressure, gives up a portion of the gas spontaneously under atmospheric pressure, thus following *Henry's Law*, according to which *the quantity of a gas dissolved in a specified quantity of liquid is proportional to pressure.* The remainder of the gas is evolved when the water is boiled. *The solubility of gases in water increases with the pressure to which they are subjected, and decreases with the temperature.*

Filtration. Solid substances in simple suspension in water may usually be separated from the water by allowing the solid particles to gradually settle to the bottom of the containing vessel, and "decanting," or pouring off, the clear liquid; or the mixture may be poured on a filter, usually made of unsized paper folded into a cone and placed for convenience in a glass funnel, in which case the solid matter will collect as a residue on the filter, and the clear liquid, or "filtrate," will pass through the funnel and may be readily collected. Thus, 1 grm. of copper oxide produces when shaken into water a black opaque mixture which, however, becomes clear and colorless when we filter it, so that it is evident that the greater part at least of the copper oxide was in suspension and not in solution. The processes of decantation and filtration do not ordinarily remove dissolved substances from solution.

Dialysis: Colloids and Crystalloids. Substances vary, however, in regard to the readiness with which their solutions pass through compact membranes like parchment and parchmentized paper. With a little apparatus called the *dialyzer*, which consists of a pocket of parchment paper and an outer vessel, it is sometimes possible to separate the solutions of substances from one another. If a solution containing common salt and egg albumen, or white of egg, in solution, is placed within the pocket of a dialyzer, while the outer vessel is filled with pure water, the common salt will gradually diffuse into the water of the outer vessel while the albumen remains in the pocket. By changing the water in the outer vessel from time to time, the salt may be gradually removed from the albumen in the pocket.

When the solution of albumen, which is typical of many similar substances separable from other substances in solution by the dialyzer, is evaporated, an amorphous jellylike mass is formed; so such substances are called *colloids*, and their solutions are *colloidal solutions* or *pseudo-solutions*. As we get on we shall find that some substances may exist either in colloidal-solution or pseudo-solution, or as insoluble gelatinous substances. In such cases we call the soluble modification of the substance its *hydrosol* and the insoluble modification its *hydrogel*. When the solution of common salt is evaporated, the salt remains in crystalline condition, and common salt is typical of many *crystalloids*.

Hydrosol: Hydrogel.

Recovery from Solution by Evaporation.

We have seen that potassium dichromate separates partially in solid form from its hot saturated solution when the water is cooled and the capacity of the water to hold the dichromate is correspondingly lessened, and incidentally, that in the process crystals are produced of a size and regularity dependent upon the rapidity of cooling. The separation of the dichromate may be hastened by actually boiling off the water, in which case the crystals will be much less perfect. Similarly, when we boil 1 grm. of copper sulphate in 15 cm.^{3} of water, it dissolves completely to a clear blue, transparent liquid from which the water may be evaporated, either spontaneously or by boiling, leaving the full amount of the original weight of copper sulphate in crystalline form, more or less perfect according to the slowness of the crystallizing process.

Supersaturated Solution.

It sometimes happens in cooling a solution to a given temperature that a greater degree of saturation is obtained than would be possible if the solution were prepared by saturating the water at the given temperature. Such solutions are *supersaturated*, and from them the excess of the solute is at once precipitated by the addition of a very little of the solid substance.

So we find that *a solid substance dissolved in water may usually be recovered by allowing the water holding it in solution to evaporate, and that the process of evaporation may be hastened by boiling the water.*

Sometimes, however, solid substances are volatile in steam from boiling water. Thus, if we should experiment with a solution of benzoic acid, we should find that, although benzoic acid is itself not volatile at the temperature of boiling water, it possesses the property of volatilizing with steam, and although some residue of benzoic acid may remain after the water has boiled away, we may be certain that we have not by this process recovered all the benzoic acid that was originally in solution. Except in the comparatively rare cases involving substances themselves volatile with steam, the process of slow or rapid evaporation may be employed to determine to what extent, if to any, a substance has been dissolved in water. Thus copper oxide is a substance which does not volatilize when boiled with water. If we evaporate on a piece of platinum foil some of the filtrate from copper oxide suspended in water, we shall find no residue remaining, and we may conclude that copper oxide is not appreciably soluble in water.

Recovery from Solution by adding a Reagent.

If we make a saturated solution of common salt in water, the addition of a little alcohol, which mixes freely with the water but which is not a solvent of the salt, will induce the "precipitation" or throwing down, that is, throwing out of solution, of a portion of the salt which was previously dissolved. The addition of a solution of hydrochloric acid to a saturated solution of salt produces an effect similar to that of the alcohol. Evidently salt is not so soluble in water containing alcohol or hydrochloric acid as it is in pure water, and the addition of these substances in suitable amount to a solution of salt will cause a precipitation of a portion of the salt by thus limiting the solvent power of the water for this particular substance. *We may frequently recover solid substances more or less completely from their solutions in water by producing a change in the solvent power of the water for individual substances by adding to the water some other liquid with which it is miscible, but which is not itself a solvent of the substance in question.*

Recovery of Liquids from Solution by Fractional Distillation.

Liquids, like solids, are sometimes recovered from solution in other liquids by changing the character of the solvent or by evaporating the solvent. When water is the solvent, however, the vapor tensions of the dissolved liquid and the water are very likely to interfere with complete separation by the simple evaporation of either the one or the other, so that frequent use is made of the special process of *fractional distillation.* This process may be readily illustrated in the recovery of alcohol from its solution in water. A convenient form of apparatus for ordinary *distillations* is a flask provided with a bent tube which is fitted by means of a rubber stopper to a large tube serving as a *condenser*, and cooled by water running through a larger tube surrounding it. The flask is closed by a stopper through which is inserted a thermometer for taking the temperature of the vapor as it passes into the condenser. On boiling a liquid in the flask the vapor passes into the condensing tube, and collects again as liquid in the receiver. The liquid thus condensed is known as the *distillate*.

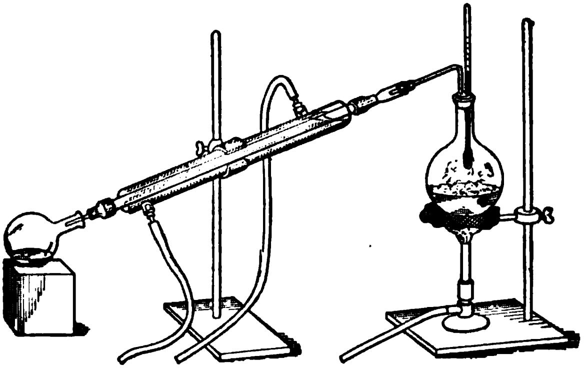

FIG. 24.—Distillation.

Water boils at 100° under normal pressure, and alcohol at 78.3° under the same conditions. When we submit a mixture of water and alcohol to distillation, the alcohol naturally boils first, passes into the condenser, and is found in the distillate; but inasmuch as the tension of water vapor is considerable at the boiling point of the mixture, the water vaporizes to some extent with the alcohol, so that while the first portions to pass over are chiefly alcohol, the distillate is never entirely free from water. As the alcohol is removed in the process of distillation, the boiling point of the mixture rises and the proportion of water vapor increases, until finally, when the temperature reaches 100°, water practically pure remains. If the successive portions or "fractions" of the distillate are collected apart and redistilled, the alcohol tends to accumulate in the low-boiling portion and the water remains in the high-boiling portions, so that an approximate separation of the alcohol from the water may finally be accomplished by this process.

For the removal of the last portions of the water from the nearly pure alcohol it is necessary to resort to special means for preventing the distillation of the water. Into the nearly pure alcohol are put bits of broken calcium oxide, or "quicklime," which has a strong affinity for water, and holds it firmly at a temperature at which alcohol boils. By distilling the liquid off the quicklime, a distillate of nearly pure or "absolute" alcohol is obtained.

Recovery of Gases from Solution. *Gases may be recovered from solution in a liquid by boiling the solution, or by diminishing the pressure under which the gas is held in the liquid.* A water solution of carbon dioxide, ordinary "soda water," charged at high pressure, gives up a part of its gas under the atmospheric pressure, another portion is liberated when we put the soda water into a flask and exhaust it by the vacuum pump, and the remainder is removed when we submit the water to continued boiling. The gradual removal of a gas from its solution in water may also be brought about by agitation in a changing atmosphere, since in this way the pressure of the gas in the atmosphere is constantly diminishing. This is well shown by passing a rapid current of air through a solution of hydrogen sulphide in water and noting the gradual disappearance of the odor characteristic of the dissolved gas.

Natural Waters. Natural waters are never perfectly pure. Even *rain water* contains gases from the air, and water flowing through the soil dissolves mineral matter. When the impurities are insignificant and agreeable to the taste the water is fresh; when the mineral impurities are considerable we have a *mineral water*, which is sometimes of medicinal value. Sea water is a very highly charged mineral water containing 30 to 40 parts of dissolved mineral matter in 1000 of water. The separation of solid, liquid, or gaseous substances from the natural water in which they are present, either in a simple state of suspension or in solution, is plainly a matter of moment.

Ordinary water, containing materials derived from the atmosphere and soil, may be purified sufficiently for ordinary chemical purposes by simple distillation and condensation of the steam, since the solid matters derived from the soil are not volatile with the steam, and the volatile impurities introduced from the atmosphere are not ordinarily objectionable in the quantities in which they remain after the distillation. The process may be easily tested on a small scale by dissolving in a little water enough potassium permanganate to color it distinctly, boiling the water, and condensing the steam. If care is taken to prevent the spurting of the liquid the condensed steam should be clear and colorless, and should leave no residue when evaporated on platinum foil.

The problem of providing palatable and wholesome water for drinking purposes or for use in the preparation of food is often a very practical question. Sometimes the natural water is good enough; sometimes a simple filtration to remove suspended matter is desirable and sufficient; sometimes, as in the case of waters contaminated with germs of disease, the water should be boiled; and sometimes when water contains harmful substances in solution it should be distilled and afterward made palatable by exposure to pure air.

Absorption or Liberation of Heat by Solution.

Thus far in our experimentation with the process of solution in water we have been able to recover from solution the original substance dissolved exactly of the composition which it possessed before solution took place. We have taken no note of the manifestation or disappearance of energy in the process. Careful observation of the phenomena will show, however, that *very considerable amounts of heat are frequently absorbed or liberated in the act of solution.* When, for example, sodium chloride, common salt, dissolves in water, heat disappears, and when calcium chloride, which we have used as a drier, dissolves, heat is evolved. If the solution of sodium chloride is evaporated spontaneously or at 100°, the original weight of sodium chloride is left, and we have no evidence in the experiment that the solution of sodium chloride in the water was more than the mere diffusion of the mass of the one throughout the mass of the other. This seems to be generally true in the case of solutions of substances which dissolve with absorption of heat. If the solution of calcium chloride is evaporated, the residue weighs much more than the original calcium chloride, even when the attempt is made to dry it at a temperature considerably above 100°, the boiling point of water. It seems obvious that calcium chloride and the water have acted upon one another chemically and entered into combination, and this appears to be the case in general when the act of solution is accompanied by liberation of heat. It does not appear, however, that the chemical combination of water and the calcium chloride is identical with the process of solution. Without attempting at present to determine whether the process of solution itself is to be regarded or not to be regarded as chemical in its nature, we may turn attention to certain phenomena in which, whether solution takes place or not, we have very definite evidence that water may enter into chemical changes with other substances.

When we put a little water upon phosphorus pentoxide contained in a porcelain crucible, much heat is evolved. The addition of more water results in the liberation of more heat, until finally the substance is dissolved in the water. The marked evolution of heat is to be taken as evidence of chemical action, and, as a matter of fact, a new substance is actually produced. Upon heating the solution until boiling ceases, a part of the water added originally may be removed, but the appearance of the cooled residue, and, when we work with weighed amounts of materials, its weight as compared with that of the phosphorus pentoxide taken, point to the fact that the water has combined with phosphorus pentoxide and is held by it firmly. Careful experimentation shows that the water cannot be removed from the new compound by heat except at a temperature sufficient to volatilize the phosphorus pentoxide as well as the water.

In like manner, when we put 15 cm.^{3} of warm water upon 50 grm. of recently prepared calcium oxide, or quicklime, broken into fragments, heat is evolved sufficient to generate steam, and to disintegrate and "slake" the lime, showing that a chemical change takes place between the water and the calcium oxide; but in this case solution does not take place, though we may if we choose take out a small portion of the residue and find it to be sparingly soluble in water. If we dry a portion of the mass on a *water bath*, — a vessel heated by boiling water, so arranged that the temperature can never rise above 100°, — and then heat the residue to a moderately high temperature, the liberation of water at the higher temperature shows that the combination existing between the water and the calcium oxide at the lower temperature may be broken and the calcium oxide formed again by heat.

So also, when we add 5 cm.^{3} of water to 5 cm.^{3} of strong sulphuric acid contained in a test-tube, a thermometer inserted in the mixture indicates a rise of temperature many degrees above the boiling point of water, but the liquid compound of the water and the sulphuric acid is not sufficiently strong to resist the decomposing action of heat, and the water may be boiled out gradually until the evolution of thick white fumes shows that the strong sulphuric acid has been reproduced.

Water of Hydration. In the action of water upon phosphorus pentoxide, calcium oxide, and sulphuric acid we have evidence of a more or less strong chemical combination of the water with the substances mentioned; but we have met with no evidence to show whether the water actually combines with these substances bodily as water, or whether the elements of water, hydrogen and oxygen, enter independently into the combination with other substances. *Whatever the true nature of the combination of water with substances may be, whether it may be removed by heat, or is not so removable, water while so combined is known as water of hydration.*

Crystallization. Sometimes the water entering into combination with a substance causes the substance to assume a definite crystalline form characteristic of that combination. For example, if we heat 5 or 10 grm. of crystallized copper sulphate in a porcelain dish, the blue powder becomes white, as the water contained in the crystals escapes in the form of steam. The blue color is restored to a portion of the white powder if we add to it a drop of water, or allow it to stand for some time in moist air; and when we dissolve the white powder in water and evaporate the solution, we obtain blue crystals, similar to those with which we originally experimented. Evidently when copper sulphate crystallizes from water it combines with water and this water of hydration necessary to the assumption by the copper sulphate of a characteristic crystalline form is *water of crystallization.* When the white "anhydrous" powder becomes blue, it combines with water, passing into the so-called blue "hydrous" or "hydrated" condition, and is minutely crystalline, but the immobility of the particles of solid powder prevents the formation of crystals visible to the eye. It is only when particles of copper sulphate are allowed to move freely, as when they are in solution, that we have a growth of crystals to visible dimensions. *Water of hydration entering into the structure of a substance in a way to determine the crystalline form is called water of crystallization, and may be removed by heat.*

Hydroxides. *When water combines with an oxide, the compound formed is called a hydroxide, and compounds which may be resolved into water and an oxide are also known as hydroxides, even though it may not be practically possible to form them by direct combination of water with an oxide.*

Thus calcium oxide, though sparingly soluble, nevertheless combines with water to form white calcium hydroxide or "slaked lime," not unlike the oxide in appearance.

Calcium Oxide + Hydrogen Oxide = Calcium Hydroxide

So also phosphorus pentoxide and water combine to form sirupy phosphorus hydroxide, or "phosphoric acid," as it is commonly called.

Phosphorus Pentoxide + Hydrogen Oxide = Phosphorus Hydroxide

Water and nitrogen pentoxide form the liquid nitrogen hydroxide known ordinarily as "nitric acid," sulphur dioxide forms with water an unstable compound which we know as "sulphurous acid," the solution of carbon dioxide in water contains also an unstable hydroxide known as "carbonic acid," while sulphur trioxide forms with water the hydroxide which we know as "sulphuric acid." These hydroxides are examples of compounds, more or less stable, made by the direct combination of water with oxides.

Some oxides are not only insoluble, but are inert in the presence of water. Such are copper oxide, zinc oxide, iron oxide; but it is possible to form hydroxides from which by the action of heat these oxides and water result. Thus, by metathesis between some suitable soluble hydroxide and a suitable compound of copper, zinc, or iron the corresponding hydroxide may be precipitated.

Copper Sulphate + Sodium Hydroxide
= Copper Hydroxide + Sodium Sulphate
Zinc Sulphate + Sodium Hydroxide
= Zinc Hydroxide + Sodium Sulphate
Iron Sulphate + Sodium Hydroxide
= Iron Hydroxide + Sodium Sulphate

The blue copper hydroxide, the white zinc hydroxide, the red iron hydroxide, are resolved into water and black copper oxide, white zinc oxide, and brown-red iron oxide, respectively, when heated.

Copper Hydroxide = Copper Oxide + Hydrogen Oxide
Zinc Hydroxide = Zinc Oxide + Hydrogen Oxide
Iron Hydroxide = Iron Oxide + Hydrogen Oxide

Decomposition of Water by Elements.

Thus far in our study of the action of water upon various substances, whether or not such action is accompanied by a chemical change, we have met with no definite evidence of the actual decomposition of the water. *It is possible, however, to show that water may be decomposed in its action upon certain* *elements at ordinary temperatures.* When, for instance, we throw a piece of sodium upon water, the sodium melts in a globule and spins about on the surface of the water, impelled by the gas evolved, until it finally disappears. If we invert a test-tube filled with water in a dish of water, and introduce under the mouth of the test-tube a small piece of sodium, contained conveniently in a bit of glass tube, the gas evolved will be collected in the test-tube and may be easily shown to be hydrogen. The hydrogen is evolved by the decomposition of water, while the oxygen formerly combined with the hydrogen enters into combination with the sodium in forming soluble sodium hydroxide. Potassium decomposes water as does sodium, forming hydrogen and soluble potassium hydroxide, but in this case the heat evolved in the action is sufficient to ignite the hydrogen liberated in contact with the air, so that it burns, again producing water. The soluble sodium hydroxide and the soluble potassium hydroxide may be found in the residues when the respective solutions are evaporated.

Sodium + Hydrogen Oxide = Sodium Hydroxide + Hydrogen
Potassium + Hydrogen Oxide = Potassium Hydroxide + Hydrogen

Some elements which will not decompose water at ordinary temperature do act upon it at temperatures sufficiently high. Thus magnesium decomposes boiling water and red-hot iron decomposes steam. In such reactions it is found that either a hydroxide or an oxide of the element acted upon by the water is formed, according to conditions, while hydrogen is liberated. When boiling water acts upon magnesium the product is insoluble white magnesium hydroxide.

Magnesium + Hydrogen Oxide = Magnesium Hydroxide + Hydrogen

When water and iron react at red heat the temperature is so high that iron hydroxide cannot exist.

Iron + Hydrogen Oxide = Iron Oxide + Hydrogen

So it appears that *the action of water upon certain elements results in its decomposition and the production of free hydrogen and hydroxides or oxides of the elements.*

Hydrolytic Action, or Hydrolysis. We find, also, upon further investigation, that *water is able to enter into metathesis with certain compounds with complete or partial formation of hydroxides or oxides and some* *compound of hydrogen.* When, for example, water acts upon phosphorus pentachloride, a compound of phosphorus and chlorine, a metathesis takes place in which the chlorine of the phosphorus pentachloride is replaced by hydrogen and oxygen, forming phosphorus hydroxide, while the remaining hydrogen of the water and the chlorine enter into combination.

Phosphorus Pentachloride + Hydrogen Oxide
= Phosphorus Hydroxide + Hydrogen Chloride

Upon boiling down the solution phosphorus hydroxide remains, while hydrogen chloride escapes with the excess of water.

Similarly, when water acts upon bismuth chloride, a part of the chlorine of the bismuth chloride is replaced by the oxygen of the water, itself combining with the remaining hydrogen of the water decomposed. In this case the resulting compound of bismuth contains bismuth, chlorine, and oxygen, and, being partly oxide and partly chloride, is called an *oxychloride.* It is insoluble and white, and is precipitated immediately when the bismuth chloride is added to the water.

Bismuth Chloride + Hydrogen Oxide
= Bismuth Oxychloride + Hydrogen Chloride

The process by which a compound is decomposed by the action of water with the formation of a hydroxide or an oxide is called hydrolysis. We shall find that hydrolytic processes play an important part among chemical reactions.

On account of its power as a solvent, its susceptibility to reaction, and its hydrolytic power, water is a most useful chemical agent. Many reactions which will not take place between dry substances are at once set up by the admission of a very little moisture. Perfectly dry chlorine and sodium, for example, fail to react; dry sulphur will not burn in dry oxygen, nor will dry phosphorus, but a mere trace of moisture serves to start reaction. Some remarkable phenomena which may be due to the separation of compounds into especially active parts or constituents, and to which we shall give attention later, are closely bound up with the chemical activity of water.

CHAPTER VII

AIR AND NITROGEN

WE know that the atmosphere in which we live contains oxygen because we have seen that element withdrawn from ordinary air by the combustion of various substances. We have found by experiment that hydrogen, magnesium, mercury, carbon, sulphur, phosphorus, copper, and iron, all possess a capacity to combine with the oxygen of the air. How much oxygen there is in a given volume of air, what are the other constituents of air, and in what proportions they are present, we have yet to discover. We may best determine the composition of air by removing the oxygen from it in such manner that we may observe and experiment with what remains.

Volumetric Analysis of Air. Of the substances which we have burned in air, phosphorus acts most energetically and quickly, and the phosphorus pentoxide formed dissolves readily in water. We may therefore analyze air volumetrically by repeating our former experiment of burning phosphorus in air, but this time so modifying the procedure that more phosphorus than will burn completely shall be ignited in air confined over water. Put a piece of phosphorus, the size of a large pea, into a small porcelain crucible, place the crucible in a small porcelain dish to keep it from being cooled by direct contact with the water, float the dish upon water, ignite the phosphorus, and cover the burning phosphorus with a bottomless bell jar, the mouth of which shall be sealed by the water in which the dish floats. As the phosphorus burns in the air inclosed in the bell jar, the white fumes of phosphorus pentoxide form,

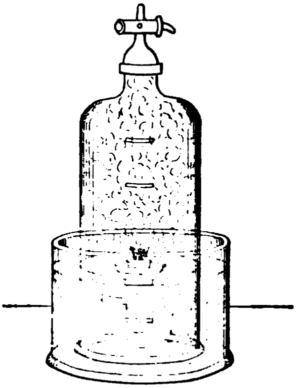

FIG. 25. — Burning Phosphorus in Air in a Confined Space.

but they soon disappear in the water, leaving a clear, colorless gas, which fills less space than was occupied by the air originally present.

We may observe roughly that *the residual gas which remains after phosphorus is burned in air occupies about four fifths of the volume of the air originally present in the bell jar.* The experiment may be managed to better advantage, however, if the phosphorus, in the form of a pellet, supported upon a coiled wire, be inserted in a long, narrow, graduated tube nearly filled with air and inverted over water, and permitted to oxidize slowly for several hours until no further reduction of the volume of the gas, as shown by the rise of water in the tube, takes place. Upon comparing the volume of air originally in the tube with that remaining after the withdrawal of the oxygen, we find, with a greater accuracy than before, that the residual gas occupies four fifths of the whole volume of air.

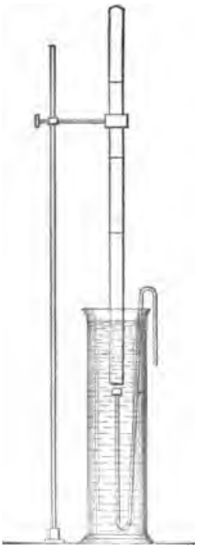

FIG. 26.— Slow Oxidation of Phosphorus in Air in a Confined Space.

Hot metallic copper will accomplish the absorption of oxygen from air quite as completely as phosphorus. A process for the preparation of considerable amounts of the residual gas, more manageable than that which involves the use of phosphorus, consists in slowly passing a current of air through a glass tube filled with copper filings and heated to redness in a tube furnace, and collecting the residual gas over water in a pneumatic trough. To apply this process to the accurate determination of the proportions of oxygen and the residual gas present in the air, we have only to devise means for measuring the volume of the air before its passage over the hot copper, and the volume of the residual gas after it has passed over the copper.

Hempel Gas Burette. A convenient apparatus for the volumetric analysis of air by this method consists of three parts: a *Hempel gas burette*, in which to measure the air and subsequently the residual gas, and which consists simply of a graduated glass tube, the lower end being connected by a rubber tube with another tube of plain glass, open at the top, to serve as a reservoir for water; a *combustion tube* to contain the copper, and which consists of a small tube of hard glass, 3 mm. in diameter and 12 cm. in length; and a *pipette*, serving as a gas holder. The two tubes of the burette are usually provided with wooden standards, and the pipette may be conveniently supported by an ordinary iron stand.

At the beginning of the experiment the gas pipette is partially filled with water, and the end of its capillary connecting tube is joined closely and tightly by a rubber connector to one end of the combustion tube, which is filled with finely divided copper, held loosely in place by a plug of shredded asbestos inserted in each end of the tube. The gas pipette and combustion tube are now clamped at a suitable height. Water is poured into the Hempel burette until a volume of air convenient for analysis remains in the graduated tube, when the stopcock is closed, and the tip of the burette above the stopcock is closely joined by a rubber connector with the free end of the combustion tube.

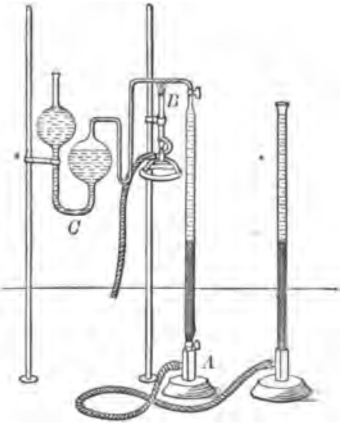

FIG. 27. — Passing a Measured Volume of Air over Heated Copper. (Hempel Burette.)

To determine definitely the amount of air present in the graduated tube, the reservoir tube is raised or lowered until the water contained in it is at the same level as the water in the graduated tube, and the volume of the air confined over the water under these conditions is read directly. The air so confined is evidently under a pressure less than the existing pressure of the outside atmosphere by an amount equal to the tension of aqueous vapor at the existing temperature. Inasmuch as we are to determine simply the relation between a given volume of air, and the volume of residual gas contained in it, it is sufficient to measure the gases at the same pressure and temperature. As the pressure and temperature of the outside air are not likely to change appreciably during the time occupied by the experiment, we need only take the precaution to make the level of the water in the graduated tube and in the reservoir the same before reading the volume of the gases on the graduated scale.

To effect the analysis of the measured volume of air, confined over water in the burette, we have only to pass it slowly from the burette, over the heated copper, through the capillary tube into the pipette, and to repass it from the pipette over the copper and into the burette, repeating the operation until it is certain that all the oxygen has united with the copper. The residual gas is finally collected in the burette, allowed to cool to the temperature of the outside air, and measured, care being taken to previously make the levels of the water in the graduated tube and in the reservoir the same. The slow passage of the air, forward and backward over the copper, may be readily effected by raising and lowering the reservoir tube, while the copper is heated with a Bunsen burner. The rapidity of the current of, air may be observed by noting the movement of the water in the gas pipette, as it is displaced from the part of the pipette nearest the combustion tube, or reënters that portion of the pipette as the gas is drawn back over the copper, the greatest care being taken to prevent the entrance of water into the combustion tube.

Let us suppose that in an actual experiment the volumetric analysis of air, conducted in the manner described, gave the following results:

Volume of air taken for analysis . .	50.00 cm.^{3}
Volume of residual gas	39.50 cm.^{3}
Volume of oxygen absorbed by copper . .	10.50 cm.^{3}

Composition of Air. These results, by a simple calculation, show us that, within the limits of experimental error, each 100 volumes of air contain 21 volumes of oxygen and 79 volumes of residual gas. The results of a great many analyses show, in fact, that *air on the average is composed volumetrically of 21 per cent. of oxygen, and 79 per cent. of residual gas*, which is found to be chiefly the element nitrogen, associated with small amounts of some other substances, to be discussed presently. The composition of air by volume was first investigated extensively by Cavendish, and later by Bunsen and others.

We have learned that a liter of oxygen weighs 1.4291 grm. at 0° and 760 mm., and it has been found that a liter of air weighs 1.2930 grm. under normal conditions, and that a liter of the residual gas weighs 1.2578 grm. under normal conditions. With a knowledge of these data and the approximate proportions by volume of oxygen and the residual gas, we may easily calculate the approximate proportions by weight in which oxygen and the residual gas are present in air.

Thus, in the present instance, we have:

Weight of 100 $cm.^3$ of air . . . . 0.1293 grm.
Weight of 21 $cm.^3$ of oxygen contained in 100 $cm.^3$ of air (21×0.0014291) . . . . . . 0.0300 grm.
Weight of 79 $cm.^3$ of the residual gas present in 100 $cm.^3$ of air (79×0.0012578) . . . . . . 0.0993 grm.
Weight of oxygen present in 100 grm. of air

$$(0.1293 : 0.03 = 100 : x)$$

$$x = \frac{0.03 \times 100}{0.1293} = \quad 23.20 \text{ grm.}$$

Weight of the residual gas—nitrogen associated with small amounts of other gases—present in 100 grm. of air

$$(0.1293 : 0.993 = 100 : x)$$

$$x = \frac{0.993 \times 100}{0.1293} = \quad 76.80 \text{ grm.}$$

So we find, by calculation from volumetric analysis, that air is composed approximately and on the average of 23 per cent. by weight of oxygen, and 77 per cent. by weight of gas which is chiefly nitrogen.

Gravimetric Analysis of Air. To analyze air gravimetrically we may draw a suitable quantity of air over heated copper, and then collect and weigh the residual gas. For this gravimetric work, however, it is desirable to employ for analysis air which has been freed from moisture and carbon dioxide, which are usually present in air in small amounts. The apparatus consists of a large flask, rendered as nearly vacuous as possible, provided with a stopcock, and connected with a combustion tube filled with finely divided copper. The combustion tube is connected with an absorption tube, containing potassium hydroxide to remove the carbon dioxide, and a calcium chloride tube to remove the moisture. The flask and the combustion tube containing the copper are weighed separately and then connected as described. The combustion tube is placed in a furnace of Bunsen burners, the copper is heated to redness, and the stopcock is then opened sufficiently to allow a current of air to pass slowly through the absorption tubes, and thence into the combustion tube, where the oxygen unites with the copper, the residual gas passing on into the flask, where it is collected. The stopcock is closed, the apparatus is cooled, and the flask and combustion tube are again weighed. The increase in the weight of the combustion tube gives the weight of oxygen absorbed, and the increase in the weight of the flask gives the weight of residual gas, chiefly nitrogen. The careful repetition of this experiment many times has shown that *100 parts by weight of air freed from carbon dioxide and moisture contain about 23 parts by weight of oxygen and about 77 parts by weight of a gas which is chiefly nitrogen;* or, in other words, that the *air contains by weight approximately 23 per cent. of oxygen, and 77 per cent. of gas chiefly nitrogen;* a result quite in accordance with the deduction of our previous calculation from the volumetric analysis of air. This gravimetric analysis of air was first accomplished by Dumas and Boussingault in 1841.

Proofs that Air is a Mixture.

It is interesting to note that *the oxygen and the gas obtained after its removal, chiefly nitrogen, are associated in the atmosphere merely as a mixture, and are not chemically combined with each other.* Of this fact there are a number of simple proofs:

(1) Although the composition of the air never varies greatly from the average, it is nevertheless not quite constant, being slightly different in different localities and in the same locality at different times.

(2) When oxygen and the gas obtained after its removal from air, chiefly nitrogen, are mixed in the proportions in which they are found in air, no temperature change or other evidence of chemical change is apparent, the mixture produced having the specific gravity 14.43, and exhibiting all the other properties of air.

(3) When air is allowed to diffuse through a porous partition, the gaseous constituents do not pass through the partition in the proportions in which they are present in the air, but according to their individual rates of diffusion. It is possible, therefore, by allowing air to pass through a porous partition, to partially remove the oxygen from the residual gas without evidence of chemical change.

(4) Similarly, when air is dissolved in water, the gaseous constituents do not dissolve in the proportions in which they are present in the air. The air found in sea water is far richer in oxygen than is atmospheric air.

Minor Constituents of Air: Water Vapor.

It is a fact of common experience that the atmosphere is charged more or less with water vapor. When *hygroscopic*, or water-absorbing, substances, such as phosphorus pentoxide or fused calcium chloride, are left exposed for some time to ordinary air, they become moist and finally lose their solid form, becoming completely dissolved in water, which, from the nature of the case, must be derived from the surrounding air. Thus we have direct evidence that seemingly dry air is not actually devoid of moisture. By passing measured volumes of air through weighed absorption tubes, containing fused calcium chloride, and determining the increase in weight of the tubes, it is possible to discover the amount of water vapor contained in the atmosphere under different conditions. In this way we find that the higher the temperature is, the more water is required to saturate a given volume of air. Thus, at 25° a liter of air may hold as much as 0.0225 grm. of water vapor, while at 0° the water vapor retained in the air is a little less than one fourth of that retained at the former temperature. The term "relative humidity," when applied to the condition of the atmosphere, refers to the degree of saturation of the air with moisture, rather than to the absolute amount of moisture present.

Carbon Dioxide. When carbon burns in a free supply of air or oxygen, a gaseous product is formed which we know as carbon dioxide. Now, since ordinary fuel consists largely of carbon, and its combustion for domestic and industrial purposes is constantly throwing products of oxidation into the air; and since, moreover, all living animals are constantly exhaling this same carbon dioxide as a product of the slow oxidation of animal tissues, it is a foregone conclusion that if we test for it by proper means we shall find *carbon dioxide* in ordinary air. We have previously noted that carbon dioxide has the property of forming a milky emulsion with limewater, and we have already employed limewater in testing for the presence of carbon dioxide. If we expose a solution of limewater, or calcium hydroxide, for some time to the air, we find that it is very soon covered with an insoluble white incrustation which, upon investigation, proves to be the same solid substance which, in suspension in the water, gave the white emulsion in the previous experiments with carbon dioxide and limewater. We may conclude, therefore, that carbon dioxide, although present in minute quantities, is nevertheless a normal constituent of the atmosphere. In ordinary air the carbon dioxide is present to an extent of 3 or 4 volumes in every 10,000, but in houses and closed spaces, where oxidation in some form or another is taking place, it is often present in larger proportions. Thus, in crowded assemblages where the ventilation is bad and the air is close and stuffy, the proportion of carbon dioxide may be as great as 10 volumes in 10,000. In such places the carbon dioxide is detrimental to health, because it retards the elimination of that gas from the lungs and prevents proper oxygenation of the blood, though the carbon dioxide itself is non-poisonous, and generally inert toward other substances. It is worthy of remark, however, that air thus vitiated with carbon dioxide is likely to contain also relatively large quantities of volatile organic matters — as well as those minute floating *organisms* which, according to our present views, have great influence upon the health of individuals and of communities.

Ammonia, Nitrogen Oxides, Inert Gases. In addition to the substances mentioned, air may contain small quantities of a compound of nitrogen with hydrogen, known as *ammonia*, together with some *nitrogen oxides*, all of which substances we shall study presently. We may also note the occurrence in air of small quantities of a modified form of oxygen known as *ozone*, and amounts of *argon* and other similar recently discovered inert gases, to the extent of nearly 1 per cent. by volume. So it appears that our atmosphere, essential to the life both of plants and animals, consists, when freed from dust and floating organisms, of nitrogen and oxygen — 78 parts by volume or 76 parts by weight of the former, and 21 parts by volume or 23 parts by weight of the latter, — besides small amounts of water vapor, carbon dioxide, ammonia, and ozone, and argon with minute traces of the very rare elements, helium, neon, krypton, and xenon. Though gaseous and so light that a cubic centimeter of it weighs but 0.00129276 grm., the air is of such depth that it exerts at the sea level in latitude 45° an average pressure sufficient to sustain a column of mercury 760 mm. high, and amounting to 1033.6 grm. per square centimeter. Under great pressure (75 atmospheres), and at very low temperature (−140°), the gaseous mixture condenses to the liquid phase, which boils under ordinary atmospheric pressure at −190°, and this "liquid air," now a commercial product, affords ready means for securing, by its evaporation, very low temperatures.

Nitrogen. Nitrogen may be obtained in pure condition by passing ammonia, a gaseous compound of nitrogen and hydrogen, over red-hot copper oxide, or by passing nitrogen oxides over red-hot copper. In the one case the combined hydrogen of the ammonia is oxidized and the water thus formed may be removed by calcium chloride or other suitable dryer; in the other case the oxygen of the nitrogen oxides is combined with copper.

Nitrogen, the largest constituent of the air, is, like oxygen, a gaseous element, colorless, tasteless, odorless. It is slightly lighter than oxygen, a liter of it weighing under standard conditions 1.2507 grm. That nitrogen is uninflammable is a matter of daily experience, and our comparative study of oxidation in air, as in pure oxygen, seems to indicate that while oxygen is distinctively a supporter of combustion, nitrogen as it exists in the air at least behaves differently. In fact, if we plunge a burning splinter of wood into a vessel containing pure nitrogen, the flame is extinguished. We may find by experiment that nitrogen is not only itself uninflammable in air or oxygen, but that it is incapable of supporting the combustion of substances which burn in air or oxygen, and is generally and to a very surprising degree inert toward other substances. It is non-poisonous, although, like many other gases, it may cause death by suffocation.

Although nitrogen is inert, and does not readily combine directly with either hydrogen or oxygen, it is nevertheless found in combination with these elements in compounds in the solid earth and in vegetable and animal bodies. By the influence of electricity, however, we may cause nitrogen to combine with hydrogen and with oxygen. Thus, if we pass an electric spark of high tension between platinum electrodes contained in a glass tube filled with a mixture of nitrogen and hydrogen, we form a colorless gas of distinctive pungent odor, a compound of nitrogen and hydrogen which bears the name *ammonia*. Similarly, if we pass the spark between platinum electrodes contained in a glass tube filled with air and held against a white background, we may observe the formation of a brownish gas, which proves to be a *nitrogen oxide*, being composed of only oxygen and nitrogen, although possessing properties which belong to neither of these elements. It is not surprising, therefore, that ordinary air, containing nitrogen and oxygen as well as water vapor which is decomposable by electricity, should contain traces of ammonia and nitrogen oxide, or compounds produced by the union of these substances with one another, or with water. The electrical disturbances which are constantly taking place in the atmosphere are amply sufficient to account for the formation of the small amount of these nitrogen compounds present in the air.

Ammonium Compounds and Nitrates.

The gaseous compounds, ammonia and nitrogen oxides, are readily absorbed by the rain water and carried to earth, where they combine with other substances, the ammonia forming the *ammonium compounds*, and the nitrogen oxides becoming *nitrates*. Among such naturally occurring compounds are *ammonium chloride*, or "sal ammoniac," and *sodium nitrate*, known as "Chili saltpeter." Nitrogen, in some form or other, is a necessary food for plants and animals. Some growing plants have the power to absorb and assimilate directly the traces of ammonia and to some extent the free nitrogen from the air, while all plants are able to absorb through their roots and assimilate the soluble ammonium compounds and nitrates which exist in the soil. Thus it happens that the tissues of plants, and of animals that feed on plants, are highly nitrogenous.

Destructive Distillation. We have, therefore, as a source from which to prepare nitrogen compounds, both the naturally occurring ammonium compounds and nitrates, and the nitrogenous vegetable and animal substances. Thus, when we heat an ammonium compound with calcium oxide or calcium hydroxide, or some similar substance, ammonia is liberated. When nitrogenous vegetable or animal substances suffer decay, or slow decomposition away from an excess of air, the odor evolved indicates the liberation of free ammonia by the disruptive process. When also we heat feathers, bone, or gelatine in a closed tube, ammonia is evolved. Thus, the ammonia and a large proportion of the ammonium compounds of commerce are produced from coal by a similar process of *destructive distillation*. On the other hand, if the decomposition of nitrogenous matter takes place slowly, under special favorable conditions, such as warmth and intermixture with a dry, porous soil containing suitable compounds of other elements, the decomposition may be influenced by a special *nitrifying ferment* in such a manner as to produce compounds of nitrogen containing oxygen and known as nitrates, such as sodium nitrate or Chili saltpeter already mentioned, which is formed naturally in Chili and Peru. The ordinary potassium nitrate or "niter" is artificially produced in the so-called *niter plantations* by closely imitating the natural process of nitrification.

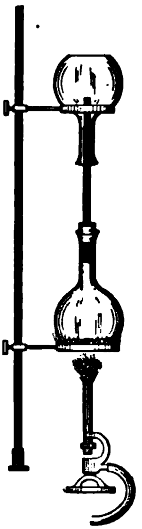

FIG. 28.—Heating Ammonium Chloride and Calcium Hydroxide.

Preparation of Ammonia. On a small scale we may obtain *ammonia* most easily by heating some one of its compounds with some substance, such as calcium oxide, which will set the ammonia free. Intermix about

20 grm. of ammonium chloride, which is one of the naturally occurring ammonium compounds, with twice its own weight of powdered dry calcium hydroxide, or slaked lime, in a round-bottomed flask of about 250 cm.^{3} capacity, and provided with a stopper and delivery tube. The ammonia is liberated slowly. It is a colorless gas, having a characteristic pungent odor. Because of the great solubility of the gas in water, it cannot be collected to advantage in a pneumatic trough, although its low specific gravity, a little more than half that of air, permits it to be collected in suitable vessels by displacing the air downward. Ammonia gas is not combustible ordinarily, although if ignited with oxygen or heated with copper oxide, it will burn with the formation of water and the liberation of nitrogen. Ammonia extinguishes a flame kindled in air, as may be seen by plunging a lighted taper into a tube filled with the gas.

Ammonium Hydroxide. The solubility of ammonia in water is demonstrated by filling a tube with the gas, and inverting it over water, when the water will rise rapidly in the tube, showing that the gas is being absorbed by the water. At ordinary temperatures and pressure, 1 cm.^{3} of water will absorb over 700 cm.^{3} of ammonia gas, and under normal conditions, 0° and 760 mm., 1 cm.^{3} of water will absorb 1148 cm.^{3} of the gas. All of the ammonia may be removed from the solution, although this affords no evidence that the water does not temporarily combine with the ammonia in such a manner as to be readily removable by heat, as was found to be true of water absorbed by sulphuric acid. The solution of ammonia in water, known as *ammonium hydroxide*, or simply as "ammonia water," is largely employed.

Ammonia, like all other gases, may be liquefied by putting it under great pressure while its temperature is kept extremely low. When the liquid ammonia is allowed to evaporate under low pressure, the cold produced by the disappearance of the latent heat of vaporization is so great that the water surrounding the vessel containing the ammonia is cooled to the freezing point. Upon this property of liquid ammonia depends its application in the arts for the manufacture of *artificial ice* and for purposes of *refrigeration*.

Analysis of Ammonia. The combustion of ammonia in the presence of copper oxide furnishes a method for the gravimetric analysis of ammonia. Thus we may pass a measured amount of ammonia over copper oxide heated to redness under such conditions that the water formed may be absorbed by calcium chloride and weighed, while the nitrogen set free may be collected and measured. The weight of the volume of ammonia taken may be calculated from the known weight of a liter of it under standard conditions, 0.7630 grm., and the weight of the nitrogen remaining may be similarly calculated from its volume and the known weight of a liter of it under standard conditions, 1.2507 grm. The experiment, if properly performed, will show that 100 parts by weight of ammonia contain 17.72 parts by weight of hydrogen and 82.28 parts by weight of nitrogen.

Ammonium Compounds. In gaseous form as well as in solution, ammonia possesses the property of coloring red litmus blue, and of destroying the properties of many acids with the production of new compounds which are usually white in color, very soluble, readily volatile when heated, and which are known as the *ammonium compounds*. The ammonia may be recovered from such compounds by heating them with calcium oxide or similar substances. The natural occurrence of ammonium compounds, as well as their production by the dry distillation of coal, and the combination of the liberated ammonia with a suitable acid, has been mentioned. We may illustrate the latter part of the process for the production of ammonium compounds in three simple instances. Thus, the floating white fumes which are generated when a jar of gaseous ammonia and a jar of the gaseous hydrogen chloride are placed mouth to mouth are solid *ammonium chloride*, produced in finely divided form. When a solution of ammonia is mixed with sulphuric acid, and the mixture is evaporated to dryness over a water bath, *ammonium sulphate* is formed, and may be recovered as a white crystalline solid. Similarly, we may prepare white crystalline *ammonium nitrate* by mixing a solution of ammonia with nitric acid, and evaporating the mixture to dryness over a water bath.

Nitrogen Oxides. We have next to consider the compounds of nitrogen and oxygen alone. The natural formation of a *nitrogen oxide* by the discharge of electricity in the air may be imitated in the laboratory with the formation of a brown gas, which may be shown to be composed of nitrogen and oxygen; but in our study of the relations of nitrogen and oxygen we may employ to better advantage the natural compounds of nitrogen, oxygen, and other substances, known as nitrates. From the *nitrates*, or from *nitric acid*, — a compound of nitrogen, oxygen, and hydrogen, which may be obtained from the nitrates by heating them with concentrated sulphuric acid, — various *nitrogen oxides* may be obtained, as we shall presently see.

Nitrogen Monoxide. When ammonium nitrate, which may be prepared by the action of ammonia upon nitric acid, is heated in a round-bottomed flask fitted with a delivery tube, the elements nitrogen, hydrogen, and oxygen, of which ammonium nitrate is composed, are rearranged in combination in such a manner that all of the hydrogen is united with part of the oxygen to form water, while the remainder of the oxygen and nitrogen are combined to form a gas which is colorless, odorless, has a sweetish taste, is somewhat soluble in water, though not sufficiently so to prevent its being collected over warm water in a pneumatic trough. The gas thus made and collected does not inflame when approached by a burning match, but, on the other hand, the wood if well kindled burns in the gas more brilliantly than in air; it mixes in air without apparent chemical change, and when inhaled in quantity produces the intoxication which gives to it the name "laughing gas," and makes it of value as an anæsthetic. Like other gases it can be liquefied and even solidified by pressure and low temperature.

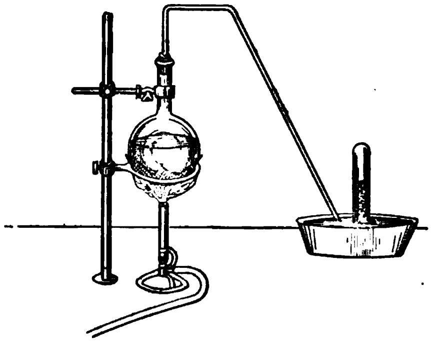

FIG. 29. — Heating Ammonium Nitrate.

The analysis of the gas, produced by heating ammonium nitrate, which may be accomplished by methods similar to those already employed for the analysis of air, shows it to contain 63.70 per cent. by weight of nitrogen, and 36.30 per cent. by weight of oxygen; or, in equivalents 28.08 of nitrogen and 16.00 of oxygen.

As we proceed we find that this compound is not the only one in which nitrogen and oxygen are found combined with one another simply, but it is, however, the only oxide of nitrogen which contains as little oxygen as 16.00 parts by weight to 28.08 parts by weight of nitrogen. And because this compound, produced by heating ammonium nitrate, contains oxygen in the smallest proportion, we give to it the distinguishing name *nitrogen monoxide*.

Nitrogen Dioxide. A second oxide of nitrogen may be prepared by acting upon dilute nitric acid with certain metals. Put into an ordinary generating flask, such as we have used for the preparation of hydrogen with sulphuric acid and zinc, some finely divided copper, cover it with warm water, and add nitric acid until the evolution of gas commences. After the first action, in which colored fumes are generated, the gas evolved is colorless, very slightly soluble in water, and may be collected in the usual manner in a pneumatic trough. When approached by a burning taper the gas does not itself inflame, and it extinguishes the taper plunged into it. Even the combustion of phosphorus, faintly kindled, may be extinguished, although curiously enough, if the phosphorus be strongly kindled and thrust into the gas, it not only continues to glow, but burns with great brilliancy, as it does in pure oxygen. Plainly, this new gas does not support feeble combustion as readily as does nitrogen monoxide, and yet, if the intensity of the combustion started in air is sufficiently great to generate enough heat, the combustion takes place in the gas quite as readily as in nitrogen monoxide. If this new gas is allowed to mix with air or with pure oxygen, we observe the production of brownish fumes of still other oxides of nitrogen, the intensity of their color depending on the relative proportions in which the gas and air or oxygen are allowed to mix.

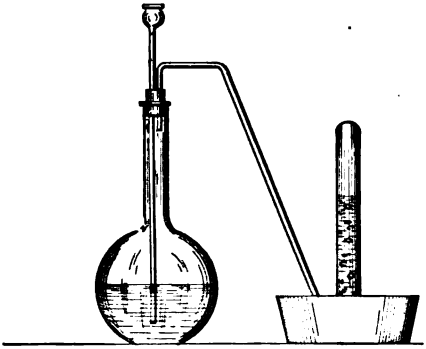

FIG. 30. — Action of Nitric Acid upon Copper.

The analysis of the gas produced by the action of dilute nitric acid upon copper turnings, effected by methods similar to those employed for the analysis of air, shows this compound to contain 46.74 per cent. by weight of nitrogen, and 53.26 per cent. by weight of oxygen, or of 28.08 parts of nitrogen to 32.00 parts of oxygen by weight. In nitrogen monoxide, as we have seen, 28.08 parts by weight of nitrogen are combined with 16.00 parts by weight of oxygen. We therefore give to our new compound, which contains twice as much oxygen to a given weight of nitrogen, the distinguishing name *nitrogen dioxide.*

It is evident from our experiment that though nitrogen dioxide contains more oxygen than nitrogen monoxide, it parts with it less easily, and tends to take on more oxygen in a fashion that nitrogen monoxide does not.

Nitrogen Trioxide. When nitrogen dioxide, prepared in the manner described, is mixed with one fourth its volume of oxygen, it combines with the oxygen, brownish red fumes of a third oxide of nitrogen being formed spontaneously. Similar colored fumes, composed largely but not entirely of this third oxide, may be readily prepared by acting upon concentrated nitric acid with arsenious oxide. When these fumes, prepared from nitrogen dioxide or liberated from nitric acid, are passed into a U-tube, cooled to — 18° by a freezing mixture of ice and salt, they are condensed to an indigo-blue liquid, which is very volatile at ordinary temperatures with re-formation of the colored fumes, extremely corrosive in its action upon the mucous membrane and upon oxidizable matter, and a strong supporter of combustion.

By analysis the reddish brown fumes, as well as the blue liquid formed by the condensation of these fumes, prepared by the union of nitrogen dioxide with one fourth its volume of oxygen, or by the action of arsenious oxide upon concentrated nitric acid, are found to be composed of 36.91 per cent. by weight of nitrogen, and 63.09 per cent. by weight of oxygen, or of 28.08 parts of nitrogen to 48.00 parts of oxygen by weight. The proportion of oxygen in this substance is exactly three times that found in nitrogen monoxide, and so we give to the new oxide the name *nitrogen trioxide.*

Nitrogen Tetroxide. When nitrogen dioxide is mixed with one half its volume of pure oxygen, brownish red fumes, similar in appearance to those produced by mixing nitrogen dioxide with one fourth its volume of oxygen, are produced spontaneously, but the fumes in this instance are found to consist principally of a fourth oxide of nitrogen, containing even a greater proportion of oxygen than is contained in nitrogen trioxide. This new oxide is present, to some extent, in the fumes liberated from nitric acid by arsenious oxide, but for its preparation in the nearly pure state we may to advantage heat dry lead nitrate, powdered and

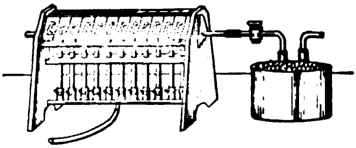

FIG. 31. — Heating Lead Nitrate and condensing the Gaseous Product.

mixed with an equal amount of ordinary sand to prevent fusion, and contained in a glass tube.

If the reddish brown fumes thus evolved are in a perfectly dry state passed into a U-tube, covered with a freezing mixture of ice and salt, they will solidify at − 20° to colorless crystals, which melt to a straw-colored liquid, darkening at higher temperatures, and boiling at + 26.7° with copious generation of a yellowish brown gas which darkens as the temperature is raised. This substance, like nitrogen trioxide, is very corrosive, a powerful oxidizer, and soluble in water.

By analysis, the reddish brown fumes, as well as the colorless crystals produced by the condensation of these fumes, formed by the union of nitrogen dioxide with one half its volume of oxygen, or by the action of heat upon lead nitrate, are found to be composed of 30.49 per cent. by weight of nitrogen, and 69.51 per cent. by weight of oxygen; that is, 28.08 parts of nitrogen to 64.00 parts of oxygen by weight. Since the proportion of oxygen here shown to be present is exactly four times the proportion of oxygen in nitrogen monoxide, the compound is named *nitrogen tetroxide.*

Nitrogen Pentoxide. We have already learned that nitric acid is composed of nitrogen together with the elements of water, — oxygen and hydrogen. Phosphorus pentoxide, a substance which we have already shown to have a great attraction for water, will act upon nitric acid chemically, removing from it hydrogen and oxygen in proportions to form water and leaving, if the temperature be kept suitably low, the remainder of the oxygen combined with the nitrogen in a fifth nitrogen oxide. This substance is white and crystalline, melts at 30°, boils at 45°, and is extremely unstable at ordinary temperatures, exhibiting a constant tendency to decompose into nitrogen tetroxide and oxygen, which makes it a very powerful oxidizer. It is readily soluble in water with the formation of nitric acid.

The analysis of the white crystals produced by the action of phosphorus pentoxide upon nitric acid shows them to be composed of 25.98 per cent. by weight of nitrogen, and 74.02 per cent. by weight of oxygen; or, of 28.08 parts of nitrogen and 80.00 parts of oxygen by weight. The proportion of oxygen contained in this substance is exactly five times that held in nitrogen monoxide, and the compound is called *nitrogen pentoxide.*

Composition of Nitrogen Oxides, by Weight.

These five oxides of nitrogen represent the entire series of the compounds of oxygen with nitrogen, and the manner in which they are put together is illustrative of a most important principle. In the following table are compared the weights of oxygen combined with a fixed weight of nitrogen in each of the nitrogen oxides:

PROPORTIONATE COMPOSITION OF NITROGEN OXIDES BY WEIGHT

	PER CENT. RATIOS		SIMPLE RATIOS	
	Nitrogen	Oxygen	Nitrogen	Oxygen
Nitrogen monoxide . . .	63.70	36.30	28.08	16.00
Nitrogen dioxide . . .	46.74	53.26	28.08	32.00
Nitrogen trioxide . . .	36.91	63.09	28.08	48.00
Nitrogen tetroxide . . .	30.49	69.51	28.08	64.00
Nitrogen pentoxide . . .	25.98	74.02	28.08	80.00

Every individual one of these oxides, possessing its own peculiar properties, is made up of oxygen and nitrogen in constant and definite proportions by weight, and when we take the series collectively it appears that the weights of oxygen combined with the same weight of nitrogen in the successive compounds of the series stand in the relation of the simple whole numbers, 1, 2, 3, 4, 5. And if we turn our attention to any two of the compounds of the series it appears that the weights of oxygen combined with a fixed weight of nitrogen in the two compounds bear to each other the relation of simple whole numbers, 1 : 2, 1 : 3, 2 : 3, etc.

Multiple Proportions.

The most careful and repeated analysis of other series of compounds has revealed the fact that in general, *when one substance forms with another substance more than one compound, the weights of the one substance relative to a given weight of the other substance in any two of the compounds bear to one another the relation of simple whole numbers.* This important generalization, known as the *Law of Multiple Proportions,* was established by John Dalton in 1803.

Individual Masses.

The kind of variation which we note in the proportions of nitrogen and oxygen in the series of nitrogen oxides suggests the idea that *the masses of these elements throughout the series represent aggregations in simple numbers of smaller individual masses which act* *as invariable units in combination.* For example, when the weights of nitrogen are taken as fixed, the weights of oxygen appear as multiples of the equivalent, 16, and in the five oxides of nitrogen for 28.08 parts of nitrogen we have successively 1, 2, 3, 4, 5 equivalents of oxygen. If an equivalent of nitrogen really represents one or more individual masses of nitrogen and an equivalent of oxygen really represents one or more individual masses of oxygen, then these numbers, 1, 2, 3, 4, 5, stand for proportionate numbers of individual masses of oxygen combined with one or more individual masses of nitrogen. Just what the relative weights of individual unit masses of oxygen and nitrogen may be in terms of the equivalent of oxygen does not now appear.

Composition of Nitrogen Oxides by Volume.

Now it will be interesting to know the proportions by volume in which gaseous nitrogen and gaseous oxygen are associated in each of these five oxides of nitrogen. A liter of nitrogen weighs 1.2507 grm. and a liter of oxygen 1.4291 grm. under normal conditions (0° and 760 mm. at sea level in latitude 45°). Knowing from the figures of analysis the percentage proportions by weight in which these gases are combined to form the various oxides, we may readily determine the simple proportions by volume under normal conditions which correspond to these proportions by weight. The relations shown by the volumetric composition of the nitrogen oxides are shown to advantage when the results of the calculations are exhibited in tabular form.

PROPORTIONATE COMPOSITION OF NITROGEN OXIDES BY VOLUME

	PER CENT. RATIOS BY WEIGHT		SIMPLE RATIOS BY VOLUME (Closely approximate)	
	Nitrogen	Oxygen	Nitrogen	Oxygen
Nitrogen monoxide . .	63.70	36.30	2	1
Nitrogen dioxide . .	46.74	53.26	2	2
Nitrogen trioxide . .	36.91	63.09	2	3
Nitrogen tetroxide . .	30.49	62.51	2	4
Nitrogen pentoxide . .	25.98	74.02	2	5

It is plainly evident that the volumes of oxygen and nitrogen associated in any given compound bear to one another very closely the relation of simple whole numbers, and that the volumes in which oxygen is united with the same volume of nitrogen in any two of the compounds likewise bear to one another very closely the relation of simple whole numbers.

Combination of Volume. A careful study of the volumetric composition of other similar series of compounds made up of gaseous substances, either elements or compounds, has shown that, in general, the volumes of gaseous substances combining to form a new substance bear to one another very closely the relation of simple whole numbers; that when one gaseous substance forms with another gaseous substance more than one compound, the volumes of the one gaseous substance relative to a given volume of the second gaseous substance in any two of the compounds bear to one another very closely the relation of simple whole numbers; and furthermore, it appears that when the product of the action of gaseous substances is also gaseous, the volume of the gaseous product bears some very simple numerical relation to the volumes of the gaseous factors.

In brief, *the volumes of gaseous substances involved as factors or products in a chemical reaction bear to one another the relation of simple whole numbers.* This is the *Law of Combination by Volume*, discovered by Gay-Lussac and Humboldt in 1805, and amplified by Gay-Lussac in 1808. We shall recur to the volume relations of gaseous substances in combination when we get farther along in our study.

CHAPTER VIII

ELECTRICAL EQUIVALENTS AND IONS

IN the course of our work we have noted that electricity is one of the forms of energy which may cause chemical change or result from chemical change. Now let us look somewhat more carefully into the electrical relations of substances.

Electrical Units. In dealing with electrical energy we recognize that the work which may be done by a current of electricity depends upon two factors. Just as the work done by falling water depends, on the one hand, upon the mass of the water, and on the other hand upon its head or fall, so when electricity passes through a circuit we may regard the total energy of the current as depending upon the quantity of electricity which fills the circuit and upon the potential under which it is driven. The quantity we measure in *coulombs* and the quantity delivered in the unit time in *amperes*, the potential in *volts*, and the resistance of a circuit to the passage of the current in *ohms*. A *coulomb* is that quantity of electricity which sets free 0.0011181 grm. of silver or 0.0000829 grm. of oxygen in an *electrolytic cell;* an *ampere* is the strength of current which delivers 1 coulomb in 1 second; an *ohm* is the resistance offered to the current by a column of mercury 106.3 cm. long and 0.01 cm.^{2} in section; a *volt* is the potential which sends 1 coulomb through a resistance of 1 ohm in 1 second, or which produces 1 ampere of current in a circuit having a resistance of 1 ohm. The total energy of the current developed in 1 second, the unit of time, is measured in *volt-amperes*, or *watts*, the product of the number of volts by the number of amperes.

Electrolysis of Hydrogen Chloride. We have seen that when water, acidulated with sulphuric acid, is submitted to the action of a suitable electric current hydrogen is liberated at one pole and oxygen is evolved at the other pole, the proportions in which these elements are liberated being those of their equivalents, 2.015 parts by weight of hydrogen to 16 parts by weight of oxygen. In like manner, when we take a solution of hydrogen chloride, hydrochloric acid, in the electrolytic cell and pass a current of electricity through it hydrogen is delivered at the one pole and chlorine, a green gas, is set free at the other pole. Chlorine is somewhat soluble in water, but after enough chlorine has been generated to saturate the solution about the pole at which the chlorine is set free it is found that hydrogen and chlorine are evolved in almost equal volumes. For every 2.015 parts by weight of hydrogen set free, 70.90 parts by weight of chlorine are evolved, and if these weights of hydrogen and chlorine, nearly equal in volume, are combined by an electric spark, or by heating to the point of ignition, hydrogen chloride is again formed. The hydrogen and chlorine are evolved in the proportion of their equivalents.

Electrolysis of Copper Sulphate. A solution of copper sulphate is decomposed similarly in the electrolytic cell with the deposition of copper at one pole and of oxygen at the other pole, in the proportions in which copper and oxygen combine to form copper oxide, 63.6 parts by weight of copper and 16 parts by weight of oxygen, or in the proportion of the equivalents of these elements.

Electrical Equivalents. It is, of course, a necessity that in the decomposition of compounds, whether by electrolysis or otherwise, the elements or complexes of elements should be liberated in the proportion of their equivalents; but it is remarkable that, as was discovered by Faraday in 1833, *when the electric current passes through different decomposable conductors arranged in series the quantities of the substances separated simultaneously are to each other in the ratio of the chemical equivalents.* So, when we arrange in sequence four cells in which are produced by the passage of a definite quantity of current measured in coulombs, hydrogen and oxygen in the first, hydrogen and chlorine in the second, copper and oxygen from copper sulphate in the third, and in the fourth copper and chlorine from melted cuprous chloride in which the equivalent of copper is twice the equivalent of that element in copper sulphate, we find that the weights produced of hydrogen, oxygen, chlorine, copper from the copper sulphate and copper from the cuprous chloride are to one another in the ratio of the equivalents of these elements in the compounds electrolyzed — namely, 2.015 for hydrogen, 16 for oxygen, 70.90 for chlorine, 63.6 and 127.2 for copper. Without the liberation of these elements in the proportions given no current passes, and since the same current passes through each cell the equivalents of the elements carry equal quantities of electricity. So it is plain that *the electrical equivalents of the elements are identical with the chemical equivalents.*

The Ions of Faraday. When electrically charged parts separated from compounds reach the electrode toward which they are directed they either give up their charges and take the ordinary forms in which we know elements and compounds or they enter into secondary reactions with the electrodes or the solvent. *The electrically charged parts that move in electrolysis Faraday called " ions."* Though the ions, elementary or complex, carry equal quantities of electricity, it appears, as we shall see, that a certain difference of potential between the electrodes is necessary in order that continuous action may take place in the electrolytic cell, and that the required difference of potential varies with the substance electrolyzed.

Electrolysis of Water. In the electrolysis of water, hydrogen is liberated at the negative pole of the electrolytic cell, — that pole which is joined to the corroded battery plate, — while oxygen is set free at the positive pole of the electrolytic cell, — that pole which is connected with the uncorroded battery plate. Since we find that electrically charged bodies attract one another when their charges are of different sign, the one positive and the other negative, and repel one another when their charges are of the same sign, both positive or both negative, we may say with reason that the hydrogen which moves to the negative pole must be positively charged, and that the oxygen which moves to the positive pole must be negatively charged. *In the electrolysis of water, the positively charged hydrogen, or positive ion, moves to the negative pole or cathode, and the negatively charged oxygen, or negative ion, moves to the positive pole or anode,* and these, giving up their charges to the electrodes, become hydrogen and oxygen in the condition in which we know these elements ordinarily.

Direction of the Current. It is sometimes convenient to discover the negative pole, or cathode, in an electrolytic cell by noting the pole at which hydrogen is evolved; or we may fix upon the positive pole, or anode, by noting the pole at which oxygen is liberated. When we speak of the *direction of the current* it is the conventionally assumed positive current to which reference is made, and we say that the current passes through the battery from the positive plate to the negative plate, through the connecting wire to the electrolytic cell, then through the electrolytic cell from the positive pole to the negative pole, and then through the wire back to the positive plate. When the connecting wire is so arranged that the current passes through it from south to north a compass needle placed above the wire is deflected to the right as we look along the wire in the direction of the current, while if the needle is placed below the wire, it is deflected to the left; and the needle will point in the reverse of these directions when the current passes from north to south. So, by noticing the deflection of a compass needle under the influence of the current passing through the connecting wire, we may determine conveniently the direction of the current and fix as positive that electrode of the electrolytic cell and that plate of the battery from which the current goes, and as negative that electrode and that plate toward which the current moves.

By means of the compass needle, or *galvanometer* as we may now call it, we may find the sign of the electrodes and so discover very easily the character of the electrical charge carried by the ions which are separated from given substances and are carrying the current, and in the amount of deflection of the needle we have an indication of the strength of the current.

In the electrolysis of water, hydrogen is the positive ion while oxygen is the negative ion.

$$\text{Hydrogen Oxide} = \overset{+}{\text{Hydrogen-ion}} + \overset{-}{\text{Oxygen-ion}}$$
$$= \text{Hydrogen} + \overset{+}{\textit{Charge to cathode}}$$
$$+ \text{Oxygen} + \overset{-}{\textit{Charge to anode.}}$$

Electrolysis of Hydrogen Chloride. When the water solution of hydrogen chloride, hydrochloric acid, is electrolyzed, hydrogen is evolved at the cathode and chlorine at the anode. Obviously in the electrolysis of hydrogen chloride, hydrogen is the positive ion and gives up its charge to the cathode, and chlorine is the negative ion and gives up its charge to the anode. Disregarding the final change which takes place when the ions give up their charges we may express the electrolysis by the equation:

$$\text{Hydrogen Chloride} = \overset{+}{\text{Hydrogen-ion}} + \overset{-}{\text{Chlorine-ion.}}$$

Electrolysis of Sodium Chloride. Sodium chloride, common salt, a compound of the elements sodium and chlorine, may be melted at a red heat and decomposed by the electric current in a suitable electrolytic cell. Under these circumstances, sodium becomes the positive ion, and moving to the negative pole, or cathode, gives up its charge, and distills off as metallic sodium, while the chlorine moves as the negative ion to the positive pole, or anode, there yields its charge, and is evolved in free condition.

When a solution of sodium chloride in water is submitted to the action of the electric current, electrolysis takes place, and chlorine is set free at the anode; but the sodium, which would naturally appear at the cathode, if there were nothing there to act upon it, enters at once, upon delivering up its electrical charge, into a secondary action upon the water and produces sodium hydroxide with liberation of hydrogen according to a reaction which we have already seen. If, however, the cathode be covered with mercury, the sodium-ion, upon giving up its charge, combines with the mercury to form an amalgam, and so is able to resist the action of the water. In this way we are able to electrolyze sodium chloride, even in its solution in water, into sodium and chlorine, the sodium separating from the sodium chloride as the positive ion, while chlorine becomes the negative ion:

$$\text{Sodium Chloride} = \text{Sodium-}\overset{+}{\text{ion}} + \text{Chlorine-}\overset{-}{\text{ion}}.$$

Electrolysis of Sodium Hydroxide.

When sodium hydroxide, a compound of sodium, oxygen, and hydrogen, which we have made by acting with metallic sodium upon water, is submitted in water solution to the action of the electric current, electrolysis takes place. We cannot expect to find free sodium in the presence of water; but if the electrolysis is performed in an apparatus provided with a mercury cathode, we may, as in the electrolysis of the sodium chloride, obtain the sodium in combination with the mercury while oxygen is set free at the anode. This action is reasonably explained by supposing that the sodium hydroxide divides into a positive sodium-ion and a negative hydrogen-oxygen-ion, hydrogen and oxygen being the other constituents of the sodium hydroxide; and that while the positive sodium-ion amalgamates with the mercury, the negative hydrogen-oxygen-ion moving to the anode gives up its charge, produces water which we do not see, and evolves so much of its oxygen as is in excess of the amount necessary to produce water with the hydrogen which it contains.

$$\begin{aligned}\text{Sodium Hydroxide} &= \text{Sodium-}\overset{+}{\text{ion}} + \text{Hydrogen-oxygen-}\overset{-}{\text{ion}}\\ &= \text{Sodium} + \text{Oxygen} + \text{Hydrogen Oxide.}\end{aligned}$$

We shall see that this view gains support when we come to study the quantitative composition of sodium hydroxide, and the way in which it breaks up in many chemical reactions.

Ionization in Electrolysis. *So we have come to recognize the phenomena of ionization in the electrolysis of chemical compounds, and the delivery of certain positive ions at the cathode or negative pole, and of certain negative ions at the anode or positive pole.* The special ions that we have thus far noted are:

Positive	Negative
Hydrogen-ion	Oxygen-ion
Sodium-ion	Chlorine-ion
	Hydrogen-oxygen-ion.

The positive ions are called *cations*, and the negative ions are known as *anions*.

Metals and Non-metals. As we proceed experimentally with the electrolysis of compounds consisting of two elements we find in general that *the distinctly characteristic metallic elements or metals, good conductors of heat and electricity, like sodium, potassium, magnesium, zinc, copper, stand together as a class with hydrogen by reason of their ability to produce positive ions, or cations, from their compounds with certain non-metallic elements like oxygen, chlorine, bromine, iodine, sulphur, which appear in the electrolysis as negative ions or anions.*

Now let us look into the action of some simple forms of voltaic cell, like the voltaic cells constituting the battery with which we first brought about the electrolysis of water. We make these batteries by immersing in water containing some corrosive agent two plates of certain different elements, kept from contact with one another within the liquid, and connected by a wire external to the liquid. We notice that one of the plates becomes corroded while the other plate remains unaffected. We have already learned that the corroded plate is called the positive plate and the uncorroded plate the negative plate, and that we may determine the sign of each plate, without going to the trouble of noting the corrosive action, by the behavior of a compass needle or galvanometer when influenced by the passing current.

The Zinc-Copper Couple. We may make a little voltaic cell by immersing in sufficiently dilute sulphuric acid a strip of zinc and a strip of copper kept from contact with one another in the liquid, and connected by a wire external to the liquid. When such a voltaic cell is put in action, the zinc is corroded by the sulphuric acid while the copper is unaffected. Upon looking into the reaction which takes place we find that sulphuric acid is broken up, hydrogen is produced and carried to the copper where it is set free, and zinc sulphate is formed in solution. We find that the current flows from the zinc to the copper in the liquid and from the copper to the zinc in the wire. Zinc is therefore the positive plate and copper is the negative plate.

$$\begin{aligned}\text{Zinc} + \overset{+}{\text{Hydrogen-ion}} + \overset{-}{\text{Sulphur-oxygen-ion}} & \\ = \text{Zinc Sulphate} + \overset{-}{\textit{Charge to zinc plate}} & \\ + \text{Hydrogen} + \overset{+}{\textit{Charge to copper plate}} &\end{aligned}$$

The Zinc-Iron Couple. We may construct similarly a little voltaic cell of zinc and iron in dilute sulphuric acid, and in this case we find that the zinc is corroded, with formation of zinc sulphate, and that hydrogen is liberated. The current flows from the zinc to the iron in the liquid, and from the iron to the zinc in the wire. The zinc is positive and the iron is negative.

We may say, therefore, that *zinc is electrically positive to both copper and iron.*

The Iron-Copper Couple. If now we construct a cell of iron and copper in dilute sulphuric acid, we find that the iron becomes the corroded plate, iron sulphate and hydrogen being formed, and that the current flows from the iron to the copper in the liquid, and from the copper to the iron in the wire. The iron is the positive plate and the copper is the negative plate, and *iron is electrically positive to copper.*

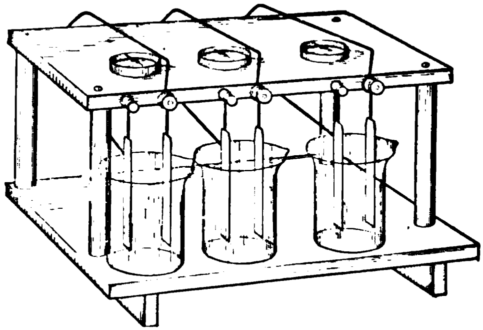

FIG. 32. — A Convenient Arrangement of the Metallic Couples.

If we compare the behavior of the three metals in the three electrical couples, we see that the zinc is clearly positive to copper, and that while in the zinc-iron couple the iron is negative to the zinc, in the iron-copper couple the iron is positive to the copper. Evidently the character of the iron as a negative or positive element is determined by its association. We see further that the electrical relations of these three elements may be shown if we arrange the elements in a series, commencing with zinc, the most positive element, and ending with copper, the most negative element. Iron, occupying the intermediate position, is negative to the element above it, and positive to the element below it.

+ Zinc
± Iron
− Copper

The Non-polarizing Cell.

In the simple type of voltaic cell which we have been using hydrogen moves from the positive plate to the negative plate, and there, adhering more or less to the negative plate, transforms it partly into a hydrogen plate, or, as it is said, "polarizes" the cell. If each plate is made to dip into a solution of a substance which may be ionized into the element of which the plate consists, as cation, and an anion, with due care to keep the two liquids from mixing, hydrogen is not a product of the action, and a *non-polarizing cell* is the result. Thus, by dipping a zinc plate into a solution of zinc sulphate contained in a jar, and a copper plate into a solution of copper sulphate contained in a porous cup set within the solution of zinc sulphate, we have an arrangement in which each metal dips into the solution of a compound of that metal with a sulphur-oxygen-$\overset{-}{\text{ion}}$, while these two solutions, of zinc sulphate and copper sulphate, are in contact and yet kept from mixing very much by the wall of the porous cup.

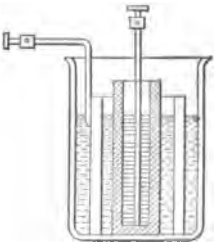

FIG. 33. — Zinc Plate in Zinc Sulphate and Copper Plate in Copper Sulphate, separated by Porous Cup. (Non-polarizing cell.)

If now the zinc plate and the copper plate are connected by a wire, the current moves from the zinc toward the copper through the liquids. In the jar zinc is corroded with formation of zinc sulphate, while in the porous cup copper is deposited upon the copper plate.

We have in the jar,

$$\text{Zinc Sulphate} = \text{Zinc-}\overset{+}{\text{ion}} + \text{Sulphur-oxygen-}\overset{-}{\text{ion}}$$

and in the cup,

$$\text{Copper Sulphate} = \text{Copper-}\overset{+}{\text{ion}} + \text{Sulphur-oxygen-}\overset{-}{\text{ion}}$$

Then, by exchange of ions and charges between the liquids, and action upon the zinc plate,

$$
\begin{aligned}
&\text{Zinc} + [\overset{+}{\text{Zinc-ion}} + \overset{-}{\text{Sulphur-oxygen-ion}}] \\
&\qquad + [\overset{+}{\text{Copper-ion}} + \overset{-}{\text{Sulphur-oxygen-ion}}] \\
&\qquad\qquad = \text{Zinc Sulphate} + \overset{-}{\textit{Charge}}\ \textit{to zinc plate} \\
&\qquad\qquad\qquad + \text{Zinc Sulphate} + \overset{+}{\textit{Charge}}\ \textit{to copper plate} + \text{Copper}
\end{aligned}
$$

The Potential of the Cell. A similar non-polarizing cell may be made by using zinc in zinc sulphate with iron in iron sulphate, and another non-polarizing cell by using iron in iron sulphate with copper in copper sulphate. Such cells while in action maintain a difference of potential between the electrodes that is nearly constant, and this difference, or what is called the *potential of the cell,* may be determined by means of a *voltmeter.*

In all such processes it is found that the reactions involve equivalents of the elements for the same quantity of electricity passing through the cell, and so are in accord with Faraday's Law ; but the work which the cell can perform for an equivalent of element involved varies with the elements and is proportional to the difference of potential between the electrodes. So it appears that *the potential of the cell measures the work done in connection with the chemical reaction in the cell.* Moreover, we find that the potential difference is greatest between the individual elements farthest apart in the series. Thus we find that the potential differences for the couples composed of the elements mentioned, in their sulphate solutions, stand as follows:

Zinc-copper	1.039 volts
Zinc-iron	0.431 volts
Iron-copper	0.608 volts

Potential Differences. Now, the physicists are able to show us that the entire differences of potential between the electrodes of any such cell are very nearly the sum of the single potential differences between the metals of the couple and the suitable solutions of their compounds constituting the cell liquids, and that these single potential differences, approximately similar for different compounds of the same elements in the cell liquids, are determinable by appropriate means. So we may make a table which shall exhibit the order and in many cases the approximate numerical values of single potentials of the metals,— the differences between the potentials of the individual metals and the potentials of the suitable solutions of their compounds taken as zero. *In this single potential series every metal is electrically positive to a metal below it, and electrically negative to a metal above it.*

DIFFERENCES IN POTENTIAL BETWEEN METALS AND SOLUTIONS OF THEIR COMPOUNDS

[Potentials of solutions = 0.]

METAL	SULPHATE Volts	CHLORIDE Volts	NITRATE Volts	ACETATE Volts
Magnesium	+1.239	+1.231	+1.060	+1.240
Aluminium	+1.040	+1.015	+0.775	——
Manganese	+0.815	+0.824	+0.560	——
Zinc	+0.524	+0.503	+0.473	+0.522
Cadmium	+0.162	+0.174	+0.122	——
Thallium	+0.114	+0.151	+0.112	——
Iron	+0.093	+0.087	——	——
Cobalt	−0.019	−0.015	−0.078	−0.004
Nickel	−0.022	−0.020	−0.060	——
Lead	——	−0.095	−0.115	−0.079
Hydrogen*	−0.238	−0.249	——	−0.150
Bismuth	−0.490	−0.315	−0.500	——
Arsenic	——	−0.550	——	——
Antimony	——	−0.376	——	——
Tin	——	−0.085	——	——
Copper	−0.515	——	−0.615	−0.580
Mercury	−0.980	——	−1.028	——
Silver	−0.974	——	−1.055	−0.991
Palladium	——	−1.066	——	——
Platinum	——	−1.140	——	——
Gold	——	−1.356	——	——

The potential of any couple made by using any two of these elements in the solutions of their compounds named is expressed by the algebraic difference of the single potentials recorded. The numerical values, and even the order in some cases where secondary chemical reactions take place apart from the main reaction, vary somewhat with change in the concentration and composition of the cell solutions. As a result of many experiments it appears that unless secondary chemical reactions intervene the potential of the metal is independent of the nature of the negative ion of the compound present in the solution.

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* Classed with the metals.

Just as the metals develop in the formation of compounds different potentials, so *different potentials are required to separate the metals from compounds by electrolysis.* It is possible, for example, to precipitate only the copper from a solution containing a copper compound and a zinc compound if the difference of potential between the electrodes is kept suitably low, and by increasing the potential difference to deposit the zinc as well as the copper.

The approximate dissociation potentials, or single potentials required to separate from their compounds various metals or cations, and also various non-metals or anions, are given in the following table, the single potential of hydrogen being fixed as 0.

Approximate Single Potentials of Ions

Cations	Volts	Anions	Volts
Zinc	+0.770	Iodine	−0.520
Cadmium	+0.420	Bromine	−0.993
Lead	+0.148	Oxygen	−1.08
Hydrogen	±0.000	Chlorine	−1.417
Copper	−0.329	Hydrogen-oxygen 2.015* 32.06*	−1.68
Silver	−0.771	Sulphur-oxygen 32.06* 64*	−1.9

From these figures for the dissociation potentials it is possible, by taking the algebraic difference of the potentials of the ions involved, to determine the potential of the current which is required to electrolyze a compound which upon ionizing gives the ions for which the data are given. Thus for the electrolysis of zinc sulphate a current showing at the electrodes a potential difference approximating $0.770+1.9$, or 2.67 volts is required, while copper sulphate may be electrolyzed with a current of which the potential is approximately $1.9-0.329$, or 1.571 volts.

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* Equivalent.

Chemical Affinities. Electricity is developed in the voltaic cells which we have studied as the result of chemical reactions which take place, as we suppose, in obedience to *chemical attractions*, or *affinities*, of elements, or complexes of elements, and between *chemical equivalents* of the elements or complexes of elements; and so the voltaic cells are machines for converting chemical energy into electrical energy. If we suppose chemical energy to be the product of a factor determined by the weight of matter affected and of a factor determined by the chemical attractions or affinities, it is reasonable to suppose that *just as, according to Faraday's Law, chemical equivalents of the reacting elements or complexes of elements — the ions — whether in the voltaic cell or in the electrolytic cell, carry equal quantities of electricity, just so they are endowed with equal quantities of chemical energy.* Then, making the quantity of electricity carried by the chemical equivalent the measure of the quantity of chemical energy, *the chemical affinity of the elements and complexes of the elements will be measured by the individual electrical potentials.* At the present time the determination of the electrical potentials is the most available means of fixing values of chemical affinities.

Replacement of Copper by Zinc. When a piece of zinc is put into a solution of copper sulphate the zinc is corroded and copper is deposited. The reaction is like that of one of the voltaic cells which we have studied, but in this case no electrical current is established, for the simple reason that the transfer of charges takes place locally between the copper and zinc in contact. In order that the reaction may produce an electric current the process of corroding the one metal and depositing the other must take place at different points in the liquid. The reaction takes place, however, in obedience to the chemical attractions and in this case, as we shall see later, chemical energy is transformed into heat. The reaction is expressed by the equation:

$$\text{Zinc} + \text{Copper Sulphate} = \text{Zinc Sulphate} + \text{Copper}$$

or, $$\text{Zinc} + [\overset{+}{\text{Copper-ion}} + \overset{-}{\text{Sulphur-oxygen-ion}}]$$
$$= [\overset{+}{\text{Zinc-ion}} + \overset{-}{\text{Sulphur-oxygen-ion}}] + \text{Copper}$$

If we consult the tables of potentials we see that the reaction has proceeded so that the cation of higher potential, the zinc, has displaced the cation of lower potential, the copper, from its combination with the anion, the sulphur-oxygen-ion, and this is quite in accord with what should take place if chemical affinity is measurable by electrical potential. We find, in general, that *the single potential series of the metals or cations is also a series which expresses the tendencies of metals or cations to combine with non-metals or anions; and that the higher a metal or cation stands in the series, the greater is its tendency to replace a lower metal or cation in a compound of the latter and a non-metal or anion.*

Replacement of Lead by Zinc.

For example, if a piece of zinc, which stands above lead in the series, is suspended in a strong solution of lead acetate, the zinc is corroded, forming zinc acetate, and the lead is deposited upon the zinc where the action takes place, forming ultimately the arborescent growth of lead crystals known as the "lead tree."

Lead Acetate + Zinc = Zinc Acetate + Lead

Replacement of Copper by Iron.

We notice in the table that iron stands above copper, and are not surprised, therefore, to find that a strip of iron dipped into a solution of copper sulphate, becomes covered with copper, while iron sulphate is formed in solution.

Copper Sulphate + Iron = Iron Sulphate + Copper

Replacement of Mercury by Copper.

So, also, if we hang a bit of copper, which stands above mercury in the series, in a solution of mercury nitrate, the liquid soon takes the color of copper nitrate in solution, while mercury is deposited upon the copper as a dark coating which takes, when rubbed with a bit of paper, the characteristic color and luster of mercury.

Mercury Nitrate + Copper = Copper Nitrate + Mercury

Replacement of Silver by Mercury.

Mercury, in turn, which stands below zinc, iron, and copper in the series, and which, accordingly, does not displace these elements from their solutions, will nevertheless displace silver from silver nitrate, since silver is below mercury in the series. Thus, a little mercury placed in a solution of silver nitrate soon becomes coated with fine crystals containing the silver in partial combination with mercury.

Silver Nitrate + Mercury = Mercury Nitrate + Silver

We find, furthermore, *that the single potential series of non-metals or anions is also a series which expresses the tendencies of the non-metals or* *anions to combine with metals or cations;* and that *the lower a non-metal or anion stands in the series, the greater is its tendency to replace a higher non-metal or anion in a compound of the latter and a metal or cation.*

Replacement of Bromine by Chlorine.

The single potential series shows that chlorine is lower in the series than bromine. When, therefore, we add chlorine, dissolved in water, to a solution of potassium bromide, we are not surprised to find that the bromine is liberated and may be collected from its solution in the water by shaking the solution with a little chloroform, which, taking the bromine away from the water, holds it in a reddish yellow solution, while the potassium chloride remains dissolved in the water.

Potassium Bromide + Chlorine = Potassium Chloride + Bromine

Replacement of Iodine by Chlorine or Bromine.

So also we might predict that either chlorine or bromine will replace iodine in potassium iodide, and this we find to be the case when we add a very little chlorine or bromine to a solution of potassium iodide. The iodine thus liberated may, like the bromine, be collected in chloroform, but its color is violet and quite characteristic.

Potassium Iodide + Chlorine = Potassium Chloride + Iodine

Potassium Iodide + Bromine = Potassium Bromide + Iodine

The greatest tendency to action comes out between the highest metals or cations and the lowest non-metals or anions.

Further investigation of the electrical potentials involved in various systems of elements is much to be desired.

CHAPTER IX

ACIDS, BASES, SALTS

We have already in the course of our study met with certain acids like hydrochloric acid, nitric acid, sulphuric acid, phosphoric acid, and carbonic acid. All these substances which we have called acids are characterized by a sharp, sour taste, more or less like that of vinegar, and all are compounds of hydrogen, and with the exception of hydrochloric acid all are hydroxides. Hydrochloric acid and carbonic acid are solutions in water of colorless gaseous hydrogen chloride and carbon dioxide respectively, while nitric acid, sulphuric acid, and phosphoric acid are colorless liquids which may be dissolved in water to form solutions more or less dilute. As we get on we shall see that these acids react more or less rapidly with certain metals like zinc and magnesium, as we have seen sulphuric acid react; and when we take note of the character of the elements associated in them with hydrogen or hydrogen and oxygen, we shall find that these associated elements are non-metallic. Neither chlorine, nor nitrogen, nor sulphur, nor phosphorus, nor carbon, possess the physical properties which characterize the metals. These compounds containing both hydrogen and non-metallic elements we call *typical acids*.

Certain other hydroxides with which we have met, though compounds of hydrogen, are very different from the typical acids. Such compounds are sodium hydroxide and potassium hydroxide. These two hydroxides are alike in being white solids, dissolving in water to form solutions which even when very dilute possess powerfully caustic properties, acting upon the skin when applied to it, and so producing a characteristic slipperiness of the skin like that produced by soap. They are also alike in being hydroxides of elements, sodium and potassium, which have the luster and other properties characteristic of metals.

Hydrogen Chloride and Sodium Hydroxide.

Now let us study more in detail the individual properties, and then the behavior toward one another, of representatives of each of these two groups of compounds. Hydrochloric acid, a member of the first group, the solution in water of the extremely soluble gaseous hydrogen chloride, may be completely volatilized by heating. Sodium hydroxide, a member of the second group, is a white solid, soluble in water, left behind as a residue when the water which dissolves it is evaporated, and able to withstand a very high temperature without decomposing or volatilizing. Both hydrogen chloride and sodium hydroxide may be analyzed and the results of the analyses may be conveniently expressed by equivalents, as shown in the following table:

COMPOSITION OF HYDROGEN CHLORIDE

	Parts by Weight
Hydrogen	2.02
Chlorine	70.90
Hydrogen Chloride	72.92

The composition of sodium hydroxide, similarly determined, is shown by the following figures:

COMPOSITION OF SODIUM HYDROXIDE

	Parts by Weight
Sodium	46.10
Oxygen	32.00
Hydrogen	2.02
	80.12

We may determine, moreover, the strength of a solution of either hydrogen chloride or of sodium hydroxide, and thus be able to know what weight of either substance we have when we weigh out or measure out a given amount of solution.

Let us now take enough of hydrochloric acid solution to contain 72.92 cgrm. of hydrogen chloride, and add to it 80.12 cgrm. of sodium hydroxide, previously dissolved in water, mix the solutions, evaporate the liquid, and examine the residue. A new substance is left which has neither the sharp taste of the hydrogen chloride nor the caustic action of the sodium hydroxide. Upon analyzing this residue we find it to consist of sodium and chlorine in the proportions by weight shown below. It is *sodium chloride.*

COMPOSITION OF SODIUM CHLORIDE

	Parts by Weight
Sodium	46.10
Chlorine	70.90
Sodium chloride	117.00

By placing side by side the figures of analysis it is possible to show what takes place when hydrogen chloride and sodium hydroxide interact in the proportions indicated. The statement may be made in the form of an equation in which hydrogen chloride and sodium hydroxide are the factors, and sodium chloride and water the products.

Hydrogen Chloride + Sodium Hydroxide = Sodium Chloride + Hydrogen Oxide

Parts by Weight		Parts by Weight		Parts by Weight		Parts by Weight	
Hydrogen	2.02	Sodium	46.10	Sodium	46.10	*Hydrogen*	2.02
		Oxygen	32.00			*Oxygen*	32.00
Chlorine	70.90	*Hydrogen*	2.02	Chlorine	70.90	*Hydrogen*	2.02
	72.92		80.12		117.00		36.04

Interaction of Hydrogen Chloride and Sodium Hydroxide.

The sodium chloride formed by the interaction of hydrogen chloride and sodium hydroxide is not a hydroxide nor a compound of hydrogen. It contains sodium and chlorine. *It appears that the hydrogen of the hydrogen chloride has been replaced by the sodium of the sodium hydroxide, and that the hydrogen thus replaced in the hydrogen chloride has combined with the hydrogen and oxygen originally in the sodium hydroxide to form hydrogen oxide or water.* The change is a metathesis, in which the identity of the hydrogen chloride and the identity of the sodium hydroxide have been destroyed. The sodium hydroxide has ***neutralised*** the hydrogen chloride, and the hydrogen chloride has ***neutralised*** the sodium hydroxide.

Neutralization.

Now if we designate the parts that move from compound to compound as "ions," as Faraday designated the parts of compounds that move under the action of the electric current, we may say that *the hydrogen-ion of the hydrogen chloride changes places with the sodium-ion of the sodium hydroxide, the sodium-ion and the chlorine-ion combining to form sodium chloride, while the hydrogen-ion combines with the hydrogen-oxygen-ion* *of the sodium hydroxide to form hydrogen oxide or water.* When we electrolyzed hydrogen chloride we saw that the hydrogen-ion was positive, and that the chlorine-ion was negative; in the electrolysis of sodium chloride we found the sodium-ion to be positive, and the chlorine-ion negative; and in the electrolysis of sodium hydroxide we found the sodium-ion to be positive and the hydrogen-oxygen-ion to be negative. We may therefore classify by their relations under electrolysis the ions which take part in the reaction between hydrogen chloride and sodium hydroxide:

POSITIVE IONS	NEGATIVE IONS
Hydrogen-$\overset{+}{\text{ion}}$	Chlorine-$\overset{-}{\text{ion}}$
Sodium-$\overset{+}{\text{ion}}$	Hydrogen-oxygen-$\overset{-}{\text{ion}}$

We may make use of this classification in writing in more simple form the equation by which this reaction is expressed:

Hydrogen Chloride +	Sodium Hydroxide =	Sodium Chloride +	Hydrogen Oxide
Hydrogen-$\overset{+}{\text{ion}}$	Sodium-$\overset{+}{\text{ion}}$	Sodium-$\overset{+}{\text{ion}}$	*Hydrogen-$\overset{+}{\text{ion}}$*
Chlorine-$\overset{-}{\text{ion}}$	*Hydrogen-oxygen-$\overset{-}{\text{ion}}$*	Chlorine-$\overset{-}{\text{ion}}$	*Hydrogen-oxygen-$\overset{-}{\text{ion}}$*

The Ions in Neutralization.

Hydrogen chloride is then a compound of hydrogen containing a positive hydrogen-ion, while in sodium hydroxide, hydrogen is a part of the negative hydrogen-oxygen-ion; the process of mutual neutralization of the hydrogen chloride and sodium hydroxide consists in the replacement of the positive hydrogen-ion of the hydrogen chloride by the positive sodium-ion of the sodium hydroxide, while the positive hydrogen-ion of the hydrogen chloride combines with the negative hydrogen-oxygen-ion of the sodium hydroxide, neutral sodium chloride and water being the products.

When the proportions in which hydrogen chloride and sodium hydroxide are mixed varies from the ratio of 72.92 parts of the former to 80.12 parts of the latter, some part of the factor in excess of the ratio indicated will be left over unneutralized. If less than 72.92 parts of the hydrogen chloride is taken to 80.12 parts of sodium hydroxide, some sodium hydroxide will be found with the sodium chloride. If more than 72.92 parts of hydrogen chloride is taken to 80.12 parts of sodium hydroxide, the amount of hydrogen chloride in excess of 72.92 parts will remain unneutralized. Plainly, 72.92 and 80.12 are equivalents of hydrogen chloride and sodium hydroxide respectively. Inasmuch, however, as hydrogen chloride is easily volatilized, any excess of it over the equivalent is not permanently retained with the sodium chloride when the mixture is evaporated. It is easily removed at the temperature of the water-bath.

Nitric Acid and Sodium Hydroxide. Now let us look into the relations toward sodium hydroxide of another member of the group of "typical acids." Nitric acid, a liquid soluble in water and volatile when heated, is found upon analysis to have the following composition:

COMPOSITION OF NITRIC ACID

	Parts by Weight
Hydrogen	2.02
Oxygen	96.00
Nitrogen	28.08
Nitric acid	126.10

When 126.10 cgrm. of nitric acid and 80.12 cgrm. of sodium hydroxide are dissolved separately in water, the solutions mixed, and the mixture evaporated, water is removed, and a new substance is left which has neither the caustic action of the sodium hydroxide nor the sharp taste of nitric acid. Upon analyzing this residue we find it to consist of sodium, oxygen, and nitrogen in the proportions shown below. It is *sodium nitrate*.

COMPOSITION OF SODIUM NITRATE

	Parts by Weight
Sodium	46.10
Oxygen	96.00
Nitrogen	28.08
Sodium Nitrate	170.18

By combining the figures of the analyses in an equation, it is possible to follow the course of action when nitric acid and sodium hydroxide interact to form sodium nitrate and water:

Nitric Acid +		Sodium Hydroxide =		Sodium Nitrate +		Hydrogen Oxide	
Parts by Weight		Parts by Weight		Parts by Weight		Parts by Weight	
Hydrogen	2.02	Sodium	46.10	Sodium	46.10	*Hydrogen*	2.02
Oxygen	96.00	*Oxygen*	32.00	Oxygen	96.00	*Oxygen*	32.00
Nitrogen	28.08	*Hydrogen*	2.02	Nitrogen	28.08	*Hydrogen*	2.02
	126.10		80.12		170.18		36.04

Interaction of Nitric Acid and Sodium Hydroxide.

It appears that the hydrogen of the nitric acid has been replaced by the sodium of the sodium hydroxide and that the exact amount of hydrogen replaced in the nitric acid has combined with the exact amount of hydrogen and oxygen originally in the sodium hydroxide to form water. The reaction is a metathesis in which the sodium hydroxide has *neutralized* the nitric acid, and the nitric acid has *neutralized* the sodium hydroxide.

Neutralization.

Looking now once more to the ions, or parts which move, it appears that the hydrogen-ion of the nitric acid changes place with the sodium-ion of the sodium hydroxide, the sodium-ion of the sodium hydroxide and the nitrogen-oxgyen-ion of the nitric acid combining to form sodium nitrate, while the hydrogen-ion of the nitric acid and the hydrogen-oxygen-ion of the sodium hydroxide combine to form water.

Upon submitting nitric acid to electrolysis, it is found that hydrogen appears at the cathode; it is a positive ion. The negative nitrogen-oxygen-ion moves to the anode, and there, entering into action with water, forms nitric acid and sets free oxygen.

Nitric acid is then a compound of hydrogen containing a positive hydrogen-ion. In the process in which nitric acid and sodium hydroxide neutralize one another, the positive hydrogen-ion of the nitric acid is replaced by the positive sodium-ion of the sodium hydroxide, sodium nitrate and water being formed:

Nitric Acid +	Sodium Hydroxide =	Sodium Nitrate +	Hydrogen Oxide
+	+	+	+
Hydrogen-ion	Sodium-ion	Sodium-ion	*Hydrogen-ion*
−	−	−	−
Nitrogen-oxygen-ion	*Hydrogen-oxygen-ion*	Nitrogen-oxygen-ion	*Hydrogen-oxygen-ion*

Interaction of Typical Acids with Sodium Hydroxide.

When we investigate the relations of the other "typical acids" to sodium hydroxide, it appears that in every case the typical acid is a compound of hydrogen containing a hydrogen-ion which is positive to the rest of the compound, and that in interaction with sodium hydroxide the positive *hydrogen-ion* and the positive *sodium-ion* are interchanged, with the consequent production of a compound of sodium with the negative ion of the acid, and water.

Sulphuric Acid	+	Sodium Hydroxide	=	Sodium Sulphate	+	Hydrogen Oxide
Hydrogen-$\overset{+}{\textit{ion}}$		Sodium-$\overset{+}{\text{ion}}$		Sodium-$\overset{+}{\text{ion}}$		*Hydrogen*-$\overset{+}{\textit{ion}}$
Sulphur-oxygen-$\overset{-}{\text{ion}}$		*Hydrogen-oxygen*-$\overset{-}{\textit{ion}}$		Sulphur-oxygen-$\overset{-}{\text{ion}}$		*Hydrogen-oxygen*-$\overset{-}{\textit{ion}}$

Phosphoric Acid	+	Sodium Hydroxide	=	Sodium Phosphate	+	Hydrogen Oxide
Hydrogen-$\overset{+}{\textit{ion}}$		Sodium-$\overset{+}{\text{ion}}$		Sodium-$\overset{+}{\text{ion}}$		*Hydrogen*-$\overset{+}{\textit{ion}}$
Phosphorus-oxygen-$\overset{-}{\text{ion}}$		*Hydrogen-oxygen*-$\overset{-}{\textit{ion}}$		Phosphorus-oxygen-$\overset{-}{\text{ion}}$		*Hydrogen-oxygen*-$\overset{-}{\textit{ion}}$

Carbonic Acid	+	Sodium Hydroxide	=	Sodium Carbonate	+	Hydrogen Oxide
Hydrogen-$\overset{+}{\textit{ion}}$		Sodium-$\overset{+}{\text{ion}}$		Sodium-$\overset{+}{\text{ion}}$		*Hydrogen*-$\overset{+}{\textit{ion}}$
Carbon-oxygen-$\overset{-}{\text{ion}}$		*Hydrogen-oxygen*-$\overset{-}{\textit{ion}}$		Carbon-oxygen-$\overset{-}{\text{ion}}$		*Hydrogen-oxygen*-$\overset{-}{\textit{ion}}$

Many other compounds of hydrogen are also known beside those which have been specifically mentioned as typical acids, all of which, containing a hydrogen-ion positive to the rest of the compound and able to exchange it for the sodium of sodium hydroxide, are to be placed in the category of acids.

Interaction of Typical Acids and Potassium Hydroxide.

Turning now to potassium hydroxide, which at the outset we classed with sodium hydroxide, we find that, like sodium hydroxide, it contains a positive metal ion, while the hydrogen is a part of a negative hydrogen-oxygen-ion, and that it reacts with the typical acids in the manner in which we have seen sodium hydroxide react. The reaction of potassium hydroxide with hydrochloric acid, for example, consists in the replacement of the hydrogen of the hydrochloric acid by the potassium of the potassium hydroxide, or, in other words, of the interchange of the positive hydrogen-ion and the positive potassium-ion, with the formation of *potassium chloride* and water, as shown in the following equation in which both the parts by weight and the ions are given:

Hydrogen Chloride	+	Potassium Hydroxide	=	Potassium Chloride	+	Hydrogen Oxide
Parts by Weight		Parts by Weight		Parts by Weight		Parts by Weight
+*Hydrogen* 2.02		+Potassium 78.30		+Potassium 78.30		+*Hydrogen* 2.02
−Chlorine 70.90		− { *Oxygen* 32.00		−Chlorine 70.90		− { *Oxygen* 32.00
		Hydrogen 2.02				*Hydrogen* 2.02
72.92		112.32		149.20		36.04

So also when potassium hydroxide and nitric acid react we have a replacement of the hydrogen of the nitric acid by the potassium of the potassium hydroxide, or an interchange of the positive hydrogen-ion and the positive potassium-ion, with formation of *potassium nitrate* and water, as shown in the equation :

Nitric Acid + Potassium Hydroxide = Potassium Nitrate + Hydrogen Oxide

Parts by Weight	Parts by Weight	Parts by Weight	Parts by Weight
+*Hydrogen* 2.02	+Potassium 78.30	+Potassium 78.30	+*Hydrogen* 2.02
– { Oxygen 96.00	– { *Oxygen* 32.00	– { Oxygen 96.00	– { *Oxygen* 32.00
Nitrogen 28.08	*Hydrogen* 2.02	Nitrogen 28.08	*Hydrogen* 2.02
126.10	112.32	202.38	36.04

Pushing further the investigation of the relations of the other typical acids to potassium hydroxide, we find that in every case the positive hydrogen-ion of the acid changes place with the positive potassium-ion of the potassium hydroxide, with the production of a compound containing potassium and the negative ion of the acid, and the formation of water.

Basic Hydroxides.

It appears, therefore, that potassium hydroxide and sodium hydroxide enter individually into many reactions with typical acids in the course of which many compounds are formed all of which contain potassium or sodium. *Potassium hydroxide is said to be the base of the potassium compounds thus formed, and sodium hydroxide is the base of the sodium compounds; sometimes we speak of them as basic hydroxides.*

Zinc Hydroxide and Aluminium Hydroxide.

Certain other hydroxides more or less resembling sodium hydroxide and potassium hydroxide, and capable of neutralizing the typical acids, are also classed as bases or basic hydroxides. Zinc hydroxide and aluminium hydroxide, for example, are such hydroxides.* Though insoluble in water, not at all caustic, and in many ways inert, they are capable of neutralizing the typical acids, and are therefore classed as bases toward these acids.

Hydrogen Chloride + Zinc Hydroxide = Zinc Chloride + Hydrogen Oxide
Hydrogen Chloride + Aluminium Hydroxide = Aluminium Chloride + Hydrogen Oxide

Interaction of Zinc Oxide and Hydrogen Chloride.

As we go on we find that certain oxides, which correspond to the basic hydroxides and consist of a positive metal ion combined with a negative oxygen-ion, are also, like the basic hydroxides, capable of neutralizing typical acids, replacing positive hydrogen-ions of the acids by other positive ions, with formation of a new compound and water. In the following equations are compared the processes of neutralizing hydrochloric acid by zinc hydroxide and by zinc oxide:

Hydrogen Chloride	+	Zinc Hydroxide	=	Zinc Chloride	+	Hydrogen Oxide
Parts by Weight		**Parts by Weight**		**Parts by Weight**		**Parts by Weight**
+*Hydrogen* 2.02		+Zinc 65.40		+Zinc 65.40		+*Hydrogen* 2.02
−Chlorine 70.90		− { *Oxygen* 32.00		−Chlorine 70.90		− { *Oxygen* 32.00
		Hydrogen 2.02				*Hydrogen* 2.02
72.92		99.42		136.30		36.04

Hydrogen Chloride	+	Zinc Oxide	=	Zinc Chloride	+	Hydrogen Oxide
Parts by Weight		**Parts by Weight**		**Parts by Weight**		**Parts by Weight**
+*Hydrogen* 2.02		+Zinc 65.40		+Zinc 65.40		+*Hydrogen* 2.02
−Chlorine 70.90		−*Oxygen* 16.00		−Chlorine 70.90		−*Oxygen* 16.00
72.92		81.40		136.30		18.02

Naturally the amount of water formed when the hydroxide is used for the neutralization is greater than that produced when the oxide is used. In the latter case all the hydrogen going into the water comes from the acid.

Basic Oxides. *Zinc oxide, like zinc hydroxide, is the base of zinc chloride. Those oxides of metals, which, like the corresponding hydroxides, are capable of neutralizing acids we call bases also; sometimes we speak of them as basic oxides.*

Acidic Oxides. *On the other hand, the oxides of many non-metals, such as the oxides of nitrogen, sulphur, phosphorus, and carbon, which combine with water to form acidic hydroxides, are called acid-form-oxides, or acidic oxides.*

To fix our ideas it will be well at the present stage to lay down in summary exactly what we mean by the general terms acid and base. *An acid is a compound containing a hydrogen-ion which is positive toward the rest of the compound; a base is a hydroxide or oxide which is capable of replacing the positive hydrogen-ion of an acid by some other positive ion, forming a new compound.*

Interaction of Hydrogen Chloride and Nitric Acid. So long as we confine our attention to the reactions which take place between typical acids on the one hand and bases on the other, the category of typical acids and the category of bases seem to be distinctly set off from one another;

but when we enter upon a study of the relations which may exist between two members of the same category the aspect of the matter begins to change. Take, for example, an examination of the mutual relation of two very characteristic typical acids, hydrochloric acid and nitric acid. When hydrochloric acid, or hydrogen chloride, and nitric acid are mixed and gently heated a reaction takes place, in which the positive hydrogen-ion of the hydrogen chloride combines with a hydrogen-oxygen-ion to form water, while a nitrogen-oxygen-ion of the nitric acid combines with the negative chlorine-ion to form a compound of nitrogen, oxygen, and chlorine.

Hydrogen Chloride + Nitric Acid = Nitrogen-oxygen-chloride + Hydrogen Oxide

Parts by Weight		Parts by Weight		Parts by Weight		Parts by Weight	
+*Hydrogen*	2.02	− { *Hydrogen*	2.02	+ { Nitrogen	28.08	+*Hydrogen*	2.02
−Chlorine	70.90	{ *Oxygen*	32.00	{ Oxygen	64.00	− { *Oxygen*	32.00
		+ { Nitrogen	28.08	−Chlorine	70.90	{ *Hydrogen*	2.02
		{ Oxygen	64.00				
	72.92		126.10		162.98		36.04

In this reaction the nitric acid breaks up into ions which are different from those which are noted when the nitric acid and sodium hydroxide enter into action. Now we have a negative hydrogen-oxygen-ion separating to combine with the positive hydrogen-ion of the hydrogen chloride, while a nitrogen-oxygen-ion, containing less oxygen than the nitrogen-oxygen-ion which forms sodium nitrate with the sodium-ion, acts as a positive ion and combines with the negative chlorine-ion. *It is plain that the nitric acid, typical acid though it is, is acting like a base toward the hydrogen chloride.* The nitrogen-oxygen chloride is a very unstable compound, decomposed at once with formation of hydrogen chloride and nitric acid by the hydrolytic action of any considerable amount of water.

Interaction of Zinc Hydroxide and Sodium Hydroxide.

In like manner we find that certain bases may act as acids toward other bases. Zinc hydroxide, as we have seen, is a base to the typical acids, furnishing a positive zinc-ion and a negative hydrogen-oxygen-ion. Sodium hydroxide, a base, will, however, act upon the less active insoluble zinc hydroxide with formation of *sodium zincate* and water, the positive sodium-ion combining with a negative zinc-oxygen-ion, while the negative hydrogen-oxygen-ion of the sodium hydroxide combines with a positive hydrogen-ion of the zinc hydroxide to form water. *The zinc hydroxide plays the part of an acid to the sodium-hydroxide.*

Sodium Hydroxide +	Zinc Hydroxide =	Sodium Zincate +	Hydrogen Oxide
Sodium-$\overset{+}{\text{ion}}$	*Hydrogen*-$\overset{+}{\textit{ion}}$	Sodium-$\overset{+}{\text{ion}}$	*Hydrogen*-$\overset{+}{\textit{ion}}$
Hydrogen-oxygen-$\overset{-}{\textit{ion}}$	Zinc-oxygen-$\overset{-}{\text{ion}}$	Zinc-oxygen-$\overset{-}{\text{ion}}$	*Hydrogen-oxygen*-$\overset{-}{\textit{ion}}$

Acidity and Basicity. *So it appears that some acids may act like bases toward other strong acids, and that certain bases may act like acids toward other strong bases.* As a general thing *the hydroxides of the non-metals are acids,* since they act readily upon hydroxides of metals like those of sodium and potassium, and with difficulty or not at all upon hydroxides of non-metals, like nitric acid and sulphuric acid. *The low hydroxides of metals are generally bases.* Thus, such hydroxides, which contain a relatively lower amount of oxygen and hydrogen than is contained in other hydroxides of the same element, interact more readily with the typical acids than with the strong basic hydroxides, while *some elements which form basic hydroxides also form higher hydroxides in which the basic tendency is less pronounced, or which must even be classed generally among the acids.* As a rule, *the lower oxides of the metals are basic oxides, while the higher oxides of the metals, like oxides of the non-metals, may be acidic oxides.*

Salts. We have seen that when hydrochloric acid and sodium hydroxide neutralize one another, sodium chloride, or common salt, is the product. *All those substances which, like common salt, result when an acid is neutralized by a base, and a base by an acid, are called salts.* Sodium chloride, sodium nitrate, potassium chloride, potassium nitrate, and the other products of the mutual neutralization of the acids and bases are salts.

The salts which we have thus far studied have been made by the action of acids upon basic hydroxides or basic oxides. As we proceed with our investigation we find that a salt may likewise result from the action of a suitable acid upon a suitable metal, by the action of an acidic oxide upon a basic hydroxide, or by the interaction of an acidic oxide and a basic oxide.

As an example of processes in which a salt is formed by the action of an acid upon a metal, we may take the experiment in which we made

Interaction of Magnesium and Sulphuric Acid.

hydrogen by the action of magnesium upon sulphuric acid. When 24.36 cgrm. of magnesium act upon 98.08 cgrm. of sulphuric acid, diluted suitably with water, 2.02 cgrm. of hydrogen are set free and 120.42 cgrm. of *magnesium sulphate* may be got from the solution upon evaporating the water, as is shown in the following equation:

Magnesium + Sulphuric Acid = Magnesium Sulphate + Hydrogen

Parts by Weight	Parts by Weight	Parts by Weight	Parts by Weight
Magnesium 24.36	*Hydrogen* 2.02	Magnesium 24.36	*Hydrogen* 2.02
	Oxygen 64.00	Oxygen 64.00	
	Sulphur 32.06	Sulphur 32.06	
24.36	98.08	120.42	2.02

It is evident that the magnesium has replaced the hydrogen of the sulphuric acid to form magnesium sulphate, while the replaced hydrogen is evolved. In general, *when a metal reacts with an acid, the metal replaces hydrogen in the acid to form a salt, and the replaced hydrogen, unless something is present upon which it can act further, is liberated.*

Interaction of Carbon Dioxide and Calcium Hydroxide.

The action of the carbon dioxide upon calcium hydroxide or calcium oxide to form *calcium carbonate* serves to illustrate the *action of acidic oxides upon bases.*

The action of carbon dioxide upon calcium hydroxide is shown in the equation:

Calcium Hydroxide + Carbon Dioxide = Calcium Carbonate + Hydrogen Oxide

Parts by Weight	Parts by Weight	Parts by Weight	Parts by Weight
Calcium 40.10	Carbon 12.00	Calcium 40.10	Hydrogen 2.02
Oxygen 32.00	Oxygen 32.00	Carbon 12.00	Oxygen 16.00
Hydrogen 2.02		Oxygen 48.00	
74.12	44.00	100.10	18.02

Interaction of Calcium Oxide and Carbon Dioxide.

When calcium oxide is heated in presence of gaseous carbon dioxide under pressure, calcium carbonate is formed, and this process typifies the production of salt by the interaction of an acidic oxide with a basic oxide.

Calcium Oxide	+	Carbon Dioxide	=	Calcium Carbonate
Parts by Weight		Parts by Weight		Parts by Weight
Calcium 40.10		Carbon 12.00		Calcium 40.10
Oxygen 16.00		Oxygen 32.00		Oxygen 48.00
				Carbon 12.00
56.10		44.00		100.10

It appears, therefore, that *salts may be formed by the interaction of an acid with a basic hydroxide, a basic oxide, or a metal; or they may be formed by the interaction of an acidic oxide with a basic hydroxide or a basic oxide.*

Interaction of Salts and Acids; Salts and Bases; Salts and Salts.

From a given salt it is, moreover, sometimes possible to form a new salt by metathesis with an acid, base, or another salt. Thus from the salt barium nitrate and the acid sulphuric acid the new salt, *barium sulphate*, is formed while nitric acid is also produced; and from the salt sodium carbonate and the base barium hydroxide a new salt, *barium carbonate*, and the base sodium hydroxide are produced; and from the two salts silver nitrate and sodium chloride are formed the two new salts, *silver chloride* and *sodium nitrate.*

Barium Nitrate + Sulphuric Acid = Barium Sulphate + Nitric Acid
Sodium Carbonate + Barium Hydroxide = Barium Carbonate + Sodium Hydroxide
Silver Nitrate + Sodium Chloride = Silver Chloride + Sodium Nitrate

Neutral Salts.

Now let us turn our attention more particularly to the composition of salts, taking up first the case of those salts which are formed when a basic hydroxide and an acidic hydroxide interact. When 72.92 cgrm. of hydrogen chloride and 80.12 cgrm. of sodium hydroxide neutralize one another the sodium chloride which is formed contains, as we have seen, no hydrogen. Similarly, when 126.10 cgrm. of nitric acid and 80.12 cgrm. of sodium hydroxide enter into action, the sodium nitrate formed contains no hydrogen. It is plain that all the hydrogen in each of these acids is replaceable by the action of the base, and has been replaced from each of these acids in the process of neutralization. It is also obvious that all the hydrogen-oxygen-ion of the base is replaceable by the action of the acid, and has been so replaced in the process of neutralization. The salt which is formed as a product of neutralization, containing neither positive hydrogen-ion nor negative hydrogen-oxygen-ion, we call a *neutral salt.* So also salts formed in other ways than by the neutralization of an acid and a basic hydroxide, and which do not contain a positive hydrogen-ion, or a negative hydrogen-oxygen-ion, are neutral salts. *A salt, however formed, which contains neither a positive hydrogen-ion nor a negative hydrogen-oxygen-ion is a neutral salt.*

Acetic Acid. In the case of certain acids, however, we find, upon making the experiment, that not all the hydrogen of the acid is replaceable by the action of a base. Thus, when 80.12 cgrm. of sodium hydroxide are neutralized by 120.06 cgrm. of acetic acid, water and *sodium acetate* are formed.

Sodium Hydroxide + Acetic Acid = Sodium Acetate + Hydrogen Oxide

The sodium acetate still contains three fourths of the hydrogen of the original acetic acid, but inasmuch as no further replacement of hydrogen in sodium acetate takes place when more sodium hydroxide is added to sodium acetate, it is plain that we must regard three fourths of the hydrogen of acetic acid as unreplaceable hydrogen. In fact, investigation shows that acetic acid is a hydroxide containing carbon, hydrogen, and oxygen in such relation that only one fourth of the hydrogen constitutes the positive hydrogen-ion and can be replaced by the action of a base, and that when one fourth of the hydrogen has been replaced, the acetic acid has been completely neutralized.

Ammonium Hydroxide. So also in the case of certain basic hydroxides, not all the hydrogen is replaceable by the action of an acid. Thus, when 70.18 cgrm. of ammonium hydroxide are acted upon by 72.92 cgrm. of hydrogen chloride, water and *ammonium chloride* are formed.

Ammonium Hydroxide + Hydrogen Chloride
= Ammonium Chloride + Hydrogen Oxide

The ammonium chloride still contains four fifths of the hydrogen of the original ammonium hydroxide, but inasmuch as no further replacement of hydrogen takes place when ammonium chloride is treated with more hydrogen chloride, we must consider four fifths of the hydrogen in ammonium hydroxide as unreplaceable by the action of an acid. The one fifth of replaceable hydrogen is a constituent of the negative hydrogen-oxygen-ion, and when this has been replaced by the action of the acid, the ammonium hydroxide has been completely neutralized.

In our consideration of the acids we have to distinguish in some cases, therefore, between the positive hydrogen-ion which is replaceable and hydrogen which is a constituent of the negative ion and not replaceable in the process of neutralization; in studying basic hydroxides, we must note in some cases the distinction between hydrogen which is replaceable in the process of neutralization, and so a part of the negative hydrogen-oxygen-ion, and hydrogen which is a part of the positive ion and unreplaceable in neutralization.

Acidic Salts.

Some acids, however, are capable of interacting with bases in such proportions that only definite portions of the replaceable hydrogen of the acid are replaced in the formation of salts. Such action as this can only take place when the proportion of base to acid is less than that necessary to effect complete neutralization of the acid. Sulphuric acid is an acid capable of reacting with a base in such manner that either the whole of its replaceable hydrogen or only half of its replaceable hydrogen, according to the available proportion of base, may be replaced. Thus when 112.32 cgrm. of potassium hydroxide and 98.08 cgrm. of sulphuric acid interact, all of the replaceable hydrogen of the sulphuric acid is replaced by potassium, with the formation of a solution from which 174.36 cgrm. of *potassium sulphate* may be obtained by evaporation. Potassium sulphate contains no hydrogen and is a *neutral salt;* we call it "neutral potassium sulphate."

Potassium Hydroxide + Sulphuric Acid = Potassium Sulphate + Hydrogen Oxide

Potassium Hydroxide		Sulphuric Acid		Potassium Sulphate		Hydrogen Oxide	
Parts by Weight		**Parts by Weight**		**Parts by Weight**		**Parts by Weight**	
+ Potassium	78.30	+ *Hydrogen*	2.02	+ Potassium	78.30	+ *Hydrogen*	2.02
− *Oxygen*	32.00	− Oxygen	64.00	− Oxygen	64.00	− *Oxygen*	32.00
Hydrogen	2.02	Sulphur	32.06	Sulphur	32.06	*Hydrogen*	2.02
	112.32		98.08		174.36		36.04

Composition of Potassium Hydrogen Sulphate.

When we act with twice as much sulphuric acid upon the same amount of potassium hydroxide as before, we find that a definite change takes place in this case also, and the solution when evaporated leaves 272.44 cgrm. of *potassium hydrogen sulphate*, which contains half the replaceable hydrogen originally present in the sulphuric acid. It is an *acidic salt*, and is called "acidic potassium sulphate."

Potassium Hydroxide + Sulphuric Acid = Potassium Hydrogen Sulphate + Hydrogen Oxide

Parts by Weight	Parts by Weight	Parts by Weight	Parts by Weight
+ Potassium 78.30	+ *Hydrogen* 4.04	+ Potassium 78.30	+ *Hydrogen* 2.02
− *Oxygen* 32.00	− Oxygen 128.00	− *Hydrogen* 2.02	− *Oxygen* 32.00
Hydrogen 2.02	Sulphur 64.12	Oxygen 128.00	*Hydrogen* 2.02
		Sulphur 64.12	
112.32	196.16	272.44	36.04

If now the 272.44 cgrm. of the acidic potassium hydrogen sulphate are treated with 112.32 cgrm. of potassium hydroxide equal to the amount employed in forming that salt, 348.72 cgrm. of neutral *potassium sulphate* are formed, together with water.

Potassium Hydroxide + {Potassium Hydrogen Sulphate} = Potassium Sulphate + Hydrogen Oxide

Parts by Weight	Parts by Weight	Parts by Weight	Parts by Weight
+ Potassium 78.30	+ Potassium 78.30	+ Potassium 156.60	+ *Hydrogen* 2.02
− *Oxygen* 32.00	− *Hydrogen* 2.02	− Oxygen 128.00	− *Oxygen* 32.00
Hydrogen 2.02	Oxygen 128.00	Sulphur 64.12	*Hydrogen* 2.02
	Sulphur 64.12		
112.32	272.44	348.72	36.04

Similar to the neutral and acidic potassium sulphates, we have the neutral *sodium sulphate* and the acidic *sodium hydrogen sulphate*, and these potassium and sodium salts are typical of neutral and acidic sulphates in general. Moreover, other acids, such as phosphoric acid and carbonic acid, are capable of forming both neutral and acidic salts. Acidic salts containing a replaceable hydrogen-ion may also be formed by the interaction of an acid and a basic oxide, or a metal. *A salt, however formed, which contains a positive hydrogen-ion replaceable by action of a base is an acidic salt.*

Basic Salts. On the other hand, certain salts formed by acting upon a basic hydroxide with an amount of acid insufficient to effect the complete neutralization of the base are known as *basic salts*. It is, however, more practicable to get such salts by a partial reversal of the process of complete neutralization rather than by attempting to partially neutralize a base by an acid. In the process of neutralization of a base by an acid water is formed, and in certain cases under certain conditions, it is possible by increasing the mass of the water present to effect a reversal of the process of neutralization by the hydrolytic action of the water. In the present state of our general information about substances it will be more convenient to adopt, for purposes of illustration, this plan of making a basic salt by reversal of the process of neutralization.

Composition of Bismuth Nitrate.

Bismuth nitrate, a colorless neutral salt, has the composition:

COMPOSITION OF BISMUTH NITRATE

	Parts by weight
Bismuth	417.00
Nitrogen	84.24
Oxygen	288.00
	789.24

Interaction of Bismuth Nitrate and Water.

When bismuth nitrate is put into a convenient volume of water, the action of the water results in forming some nitric acid and a new substance. This substance, which is insoluble in water, contains less nitrogen and oxygen than was contained in the neutral bismuth nitrate, but contains hydrogen evidently derived from the water; we call it *bismuth hydroxynitrate*; it is a *basic salt*. We find that the following equation expresses the reaction under certain definite conditions:

Bismuth Nitrate + Hydrogen Oxide = Bismuth Hydroxynitrate + Nitric Acid

Parts by Weight		Parts by Weight		Parts by Weight		Parts by Weight	
+ Bismuth	417.00	+ *Hydrogen*	4.04	+ Bismuth	417.00	+ *Hydrogen*	4.04
– { Nitrogen	28.08	– { *Oxygen*	64.00	– { Nitrogen	28.08	– { Nitrogen	56.16
Oxygen	96.00	*Hydrogen*	4.04	Oxygen	96.00	Oxygen	192.00
– { Nitrogen	56.16			– { *Oxygen*	64.00		
Oxygen	192.00			*Hydrogen*	4.04		
	789.24		72.08		609.12		252.20

In this hydrolytic action of water some negative nitrogen-oxygen-ions of the bismuth nitrate are replaced by negative hydrogen-oxygen-ions of water, and combine with positive hydrogen-ions of water to make nitric acid; and an insoluble basic salt, partly nitrate and partly hydroxide, and called bismuth hydroxynitrate is formed. The basic bismuth nitrate, formed in the manner described, contains hydrogen-oxygen-ions replaceable by nitric acid when used in quantity sufficient to overbalance the hydrolytic action of the great mass of water. When we add to the liquid containing the insoluble basic bismuth hydroxynitrate in suspension a suitable amount of nitric acid, a clear solution is obtained.

Bismuth hydroxynitrate stands as a type of many basic salts the characteristic of which is that they contain hydrogen-oxygen-ions and may be further neutralized by the action of acids. *A salt, however formed, which contains a negative hydrogen-oxygen-ion replaceable by the action of an acid is called a basic salt.*

Proportionate Composition of Neutral, Acidic, and Basic Salts.

It is evident that the neutral salt formed by the interaction of an acid and a base contains in the complex, consisting of a characteristic negative ion of the acid and the characteristic positive ion of the base, enough oxygen to form a basic oxide and an acidic oxide with both these ions. For example, calcium carbonate, — a neutral salt, the formation of which we have studied, — consists of calcium, carbon, and oxygen in the exact proportions to produce calcium oxide and carbon dioxide, from which oxides, we have seen, calcium carbonate may be formed. Similarly, it will be found upon investigation that many neutral salts contain their elementary constituents in the proportions to form an acidic oxide and a basic oxide, and in many instances such salts may be decomposed into these two oxides by suitable means.

In acidic salts the proportion of the acidic oxide to the basic oxide is greater than in the corresponding neutral salts, and in basic salts the proportion of the basic oxide to the acidic oxide is greater than the corresponding neutral salts.

Thus, in the acidic potassium hydrogen sulphate and the neutral potassium sulphate we have the equivalent proportions of the basic oxide and acidic oxide shown in the following figures:

		Potassium Hydrogen Sulphate (Acidic Salt)	Potassium Sulphate (Neutral Salt)
		Parts by Weight	Parts by Weight
Potassium oxide	Potassium 78.30 Oxygen 16.00 94.30	94.30	94.30
Sulphur trioxide	Sulphur 32.06 Oxygen 48.00 80.06	160.12 (2 × 80.06)	80.06
Hydrogen oxide	Hydrogen 2.02 Oxygen 16.00 18.02	18.02	—
		272.44	174.36

The proportions of the basic oxide to the acidic oxide in basic bismuth hydroxynitrate and neutral bismuth nitrate are also shown: —

			Bismuth Hydroxy-nitrate (Basic Salt)	Bismuth Nitrate (Neutral Salt)
			Parts by Weight	Parts by Weight
Bismuth oxide	Bismuth	417.00	465.00	465.00
	Oxygen	48.00		
		465.00		
Nitrogen pentoxide	Nitrogen	28.08	108.08	324.24
	Oxygen	80.00		(3 × 108.08)
		108.08		
Hydrogen oxide	Hydrogen	2.02	36.04	——
	Oxygen	16.00	(2 × 18.02)	
		18.02	609.12	789.24

Hydroxy-salts, Oxysalts. Since acidic salts and basic salts contain hydrogen and oxygen in the proportions to form water, such salts are sometimes called *hydroxysalts*. From such hydroxysalts, either acidic or basic, *oxysalts* may be derived by separation of water. Thus, by the removal of water from acidic potassium hydrogen sulphate by heat, *potassium disulphate*, an oxysalt, is formed, and by removing the water from basic bismuth hydroxynitrate a *bismuth oxynitrate* would be formed. An inspection of the figures of analysis given above shows that these oxysalts contain the basic oxide and acidic oxide in the same proportions in which they existed in the acidic potassium sulphate and basic bismuth nitrate, respectively. *Such oxysalts are therefore classed as acidic salts and basic salts with the hydroxysalts to which they are related.*

Oxy-hydroxides, Anhydrides. Acidic and basic hydroxides may frequently be dehydrated in like manner with the production of *oxyhydroxides* or even oxides. Oxides derived from hydroxides by dehydration are sometimes called *anhydrides*.

Indicators. When the reagents which produce salts are mixed in undetermined proportions, neutral salts, or acidic salts, or basic salts, or mixtures of salts, or salts mixed with an excess of base or of acid left over, may be produced, according to the circumstances of the case. In many cases experiments with weighed materials and careful analysis of the products formed are necessary to determine the course of the reaction. In some such cases we can make advantageous use of certain substances called *indicators*, which enable us to follow the course of reactions by means of color changes.

Use of Litmus. We may frequently employ for such a purpose certain dyes, of which *litmus* is one most suitable. The behavior of litmus in the presence of soluble hydroxides is interesting. If we color a little water with litmus and then add to the solution some of the very soluble sodium hydroxide or potassium hydroxide, or of the sparingly soluble calcium hydroxide, the claret color of the litmus changes to blue. Magnesium hydroxide, though very slightly soluble, has a similar effect on litmus. *Thus we find that certain basic hydroxides of varying degrees of solubility turn litmus blue.* When we add hydrochloric acid, nitric acid, or sulphuric acid to a solution of litmus, the claret color of the litmus is turned to red, and a similar effect is produced on litmus by phosphoric acid, and to a less degree by carbonic acid. *Certain acidic hydroxides turn litmus red.*

Since certain bases turn litmus blue and certain acids turn litmus red, we may, by the use of litmus as an indicator, follow the course of a reaction between such bases and acids. Thus, if we dissolve in a quantity of water containing a little litmus a given weight of potassium hydroxide, we shall have a blue solution. If now to this solution we add slowly nitric acid, the blue color will disappear when the exact amount of nitric acid has been introduced that is necessary to neutralize the potassium hydroxide, and the least amount of nitric acid in excess will color the solution red. A little more potassium hydroxide will restore the blue color, which may be again changed to red by the nitric acid, and the alteration of color may be continued indefinitely. With extreme care to use very dilute reagents and to add them very gradually, it is possible to obtain the original claret color of the litmus, or the "neutral tint" as it is called. Such a solution brought carefully to the neutral color of the litmus yields, on evaporation, potassium nitrate. In case 112.32 cgrm. of potassium hydroxide are used, 126.10 cgrm. of nitric acid will be required for the neutralization, and 202.38 cgrm. of potassium nitrate will be obtained in the residue. We might, in like manner, study, by means of an indicator, the course of the reaction between potassium hydroxide and sulphuric acid, or the reaction between sodium hydroxide and either nitric acid or sulphuric acid, or, in fact, the reaction between any strong base and any strong acid.

It is evident, however, that an indicator may be thus employed only when the salts formed have no action upon the indicator. Thus, the salts potassium nitrate and potassium sulphate possess no action upon litmus, and neither do sodium nitrate and sodium sulphate. Most neutral salts which are formed by the interaction of a strong base and a strong acid possess no action on litmus. On the other hand, some neutral salts are more or less susceptible to hydrolytic action, and the hydroxides thus formed may differ in their power to affect litmus. Thus, potassium carbonate and potassium zincate, which are hydrolyzed with the formation in each case of a strong base and a weak acid, turn litmus blue; while zinc sulphate and copper sulphate, which are hydrolyzed with the formation of a strong acid and a weak base, turn litmus red. Furthermore, we even find some acidic salts and some basic salts, in composition part acid or part base, which do not act regularly upon litmus. Thus, while potassium hydrogen sulphate turns litmus red, potassium hydrogen carbonate turns litmus blue. *The formation in solution of salts which by themselves affect the color of litmus solution cannot be accurately followed by the use of litmus as an indicator.* In general, if we wish to know to what extent the replaceable hydrogen of an acid has been replaced by another element to form a salt, in a reaction with which we are not familiar, we must submit the product of such action to analysis.

CHAPTER X

ACTION AND EQUILIBRIUM

Energy and Chemical Action.

THE possibility and the progress of chemical change within a given substance, or between substances, depend first upon the affinities or natural tendencies to action of the elements. Many elements and many compounds show a natural inclination to act upon one another when conditions are favorable. Hydrogen and oxygen combine to form water, copper and oxygen combine to make copper oxide, sodium hydroxide and hydrogen chloride interact to form sodium chloride and water; and many other examples of chemical action between elementary substances or between compounds have presented themselves in the course of our previous study. The tendency to interact is not, however, a universal characteristic of substances. Thus, the element fluorine, while exceedingly reactive toward many substances, elementary and compound, refuses to form compounds with oxygen; and no one of the newly discovered gaseous elements — helium, neon, argon, krypton, and xenon — has been combined with another element. *Even when substances possess a natural inclination to interact under favorable conditions, the application of energy from outside the system, or the establishment of suitable conditions as to energy, is frequently necessary to bring out the inherent capacities for action.* Thus, the gases hydrogen and oxygen may be mixed and kept mixed indefinitely without the slightest formation of water until the passage of an electric spark through some part of the mixture, or the raising of the temperature of some part of the mixture, brings in enough outside energy to induce the combination of the hydrogen and oxygen at the point of electrification or ignition, when the heat liberated in such combination is sufficient to propagate the action throughout the entire mass of mixed gases. Heat, light, electricity, and mechanical energy are, as we have seen, forms of energy capable of bringing out the latent affinities of substances.

Dissociation of Mercury Oxide. In many chemical changes action goes on steadily under defined conditions of energy until it ceases for lack of material. When mercury oxide is heated, it decomposes steadily into mercury and oxygen until no more of the original mercury oxide remains.

Mercury Oxide = Mercury + Oxygen

Combination of Magnesium and Oxygen. Similarly, when magnesium is heated in oxygen, magnesium oxide is formed.

Magnesium + Oxygen = Magnesium Oxide

The product of the oxidation, magnesium oxide, is stable at the temperature at which the oxidation takes place; that is, it does not tend to give off oxygen and reproduce magnesium. When magnesium and oxygen are heated together in a closed space, the action goes on until either the magnesium has been all oxidized or until the supply of oxygen has been exhausted. The action proceeds until one or other of the factors entering into action has been used up.

Reduction of Copper Oxide by Hydrogen. The reduction of copper oxide by hydrogen at a moderately high temperature goes on to complete reduction of the copper. When copper oxide is heated in a glass tube through which hydrogen is passed, the copper oxide is reduced to copper, while the water formed escapes as steam.

Copper Oxide + Hydrogen = Hydrogen Oxide + Copper

If we were to attempt to reverse this reaction and make the hydrogen oxide or water act upon the copper to produce copper oxide and hydrogen, we should find that, while copper and water may be made to react slightly at extraordinarily high temperatures, the copper is not at a moderately high temperature in a condition of chemical activity, and fails to react appreciably with the water at temperatures reached under the conditions of heating in a glass tube. Under the conditions of the reduction of copper oxide by hydrogen there is no apparent tendency toward a reversal of the reaction, with formation of copper oxide and hydrogen. Even if we were to heat the copper oxide and hydrogen in a closed tube, so that the water produced could not escape but remained in contact with the copper, the reaction between the hydrogen and the copper oxide would proceed to completion; that is, it would go on until either no copper oxide or no hydrogen remained.

Complete and Incomplete Chemical Changes.

A chemical change in a given system is *complete* when, having proceeded continuously in a given direction, at a greater or less rate of speed with a continuous increase in the quantity of the products and a corresponding decrease in the quantity of the factors, one or more of the factors is exhausted, and the change stops merely for want of more material; on the other hand, a chemical change in a given direction is *incomplete* when increase in the quantity of the products and decrease in the quantity of factors are arrested before one or more of the factors is exhausted. *Under definite conditions of energy, an established reaction which results in the formation of a product inactive under the conditions, and so incapable of setting up a reverse action, is a complete reaction, that is, it continues to take place until one of the factors is exhausted.*

Inactive Product.

Reduction of Iron Oxide by Hydrogen.

Many reactions, however, do not proceed to completion. We have seen that when we heat iron oxide in a current of hydrogen, iron is formed and water is produced. If we take care to lead away the steam as fast as it is formed, the reaction continues with the formation of iron and water and the disappearance of iron oxide and hydrogen, so long as the proper conditions are maintained and neither the iron oxide nor the hydrogen is exhausted.

Reduction of Hydrogen Oxide by Iron.

On the other hand, when we heat iron in a current of hydrogen oxide vapor, or steam, and continuously remove the liberated hydrogen, iron oxide and hydrogen continue to be formed under these conditions until either the iron or the steam is exhausted.

If now we vary our procedure in the reduction of iron oxide by hydrogen so that we may work with suitable proportions of iron oxide and hydrogen, contained in a system to which nothing is added and from which nothing is removed during the course of the reaction, we shall have a different state of affairs. Thus, if we heat iron oxide and hydrogen in a sealed tube, part of the iron oxide will at once be reduced to iron by the hydrogen.

Iron Oxide + Hydrogen = Hydrogen Oxide + Iron

Reversed Reaction.

But the transformation can never be more than partial, for since the products remain in the system under conditions of chemical activity, a *reverse reaction* sets in, by which hydrogen oxide is reduced to hydrogen by the iron,

Hydrogen Oxide + Iron = Iron Oxide + Hydrogen

Balanced Action. and *we finally have a balanced action in which the system is in a condition of chemical equilibrium, both the direct and the reverse reactions taking place in the same system simultaneously.* We may represent such a condition of affairs by an equation,

$$\text{Iron Oxide} + \text{Hydrogen} \rightleftarrows \text{Hydrogen Oxide} + \text{Iron}$$

Similarly, when we heat iron and hydrogen oxide vapor, or steam, in a closed tube, part of the steam is reduced to hydrogen by the iron, but the action can never be complete to the point of using up all the steam; for here, as in the previous case, the reverse reaction between the products, the hydrogen and the iron oxide, is set up, resulting in a balanced action and condition of equilibrium.

$$\text{Hydrogen Oxide} + \text{Iron} \rightleftarrows \text{Iron Oxide} + \text{Hydrogen}$$

The reaction between iron oxide and hydrogen and that between hydrogen oxide and iron are typical of many reactions which in a closed system are reversible and incomplete. *In general, when the products of reactions within a closed system are chemically active, the reaction is reversible and incomplete and results ultimately in balanced action and chemical equilibrium.*

Concentration Action, or Mass Action. The condition of equilibrium is determined by a principle suggested a century ago by Wenzel, affirmed later by Berthollet, formulated by Guldberg and Waage, and now known as the law of concentration action, or law of "mass action." According to this principle of action, *equilibrium in the interaction of substances depends not only upon the affinities involved, but also upon the concentrations or masses of active substances in the unit volume.*

If, for example, the relations of four substances A, B, A', and B', involved in a reversible reaction, are as shown by the expression

$$A + B \rightleftarrows A' + B',$$

the forward tendency of the reaction is proportional to the product of the number of equivalents of A and B in a given volume into a coefficient of affinity k, acting between A and B, while the reverse tendency of the reaction is proportional to the product of the number of equivalents of A' and B' in the given volume into a coefficient of affinity k', acting between A' and B'. Then, if p, q, p', q' be the number of equivalents of A, B, A', B', respectively, present in the given volume for the case of equilibrium,

$$kpq = k'p'q'$$

and the quantities $\frac{p'}{p}$ and $\frac{q'}{q}$ represent the proportions, respectively, of the equivalents of A' produced from A and of B' from B.

By determining experimentally, as may be done in many cases, the numbers of the equivalents p, p', q, q' for some simple proportion of A, A', B, B' in a condition of equilibrium, the relation between the affinity coefficients k and k' is discovered, and $\frac{k}{k'}$ once known, it is possible to deduce the condition of equilibrium for any initial proportions of the four substances.

The velocity of reactions may also be discussed in relation to the principle of concentration action. The velocity with which a reaction progresses may be viewed as the resultant of a struggle between the tendencies to action in opposite directions. If we represent by v and v' the velocities in opposite directions, then we have for these two velocities in terms of mass action, $v = kpq$, $v' = k'p'q'$, and for V, the resultant and observed velocity,

$$V = v - v' = kpq - k'p'q'.$$

In case of equilibrium the velocities are equal and

$$kpq = k'p'q'.$$

In the case of a complete reaction, as when a product is removed from the system, the reverse velocity is 0, and the measured velocity is the product of the number of active equivalents into the affinity coefficient.

$$V = kpq$$

Based upon the principle of concentration action, expressions may be developed for the discussion of reactions in which a single substance is active and undergoes change in concentration, as when cane sugar is hydrolyzed to inactive products, or of reactions in which two or more substances undergo change in concentration. According to the form of the expression which proves applicable to the experimental investigation of a given reaction it is possible to decide whether the reaction involves one active substance and is of the *first order*, as is said, or involves more than one substance and is of the *second order* or perhaps the *third order*.

Increase and Decrease of the Active Mass.

Taking up now the consideration of a concrete case, let us look once more at the reversible reaction which takes place between hydrogen and iron oxide. When we bring together iron oxide and hydrogen in a closed space and heat the mixture, the two substances thus brought under conditions of chemical activity commence to interact with the formation of iron and hydrogen oxide, and the production of these substances continues so long as the system remains under the proper conditions. Now, since at the start there is no hydrogen oxide nor iron in the system at all, no reverse action between these substances is at first possible; but just as soon as the smallest amounts of these products are formed by the direct action, the reverse action commences, hydrogen oxide and iron interacting to form iron oxide and hydrogen. When the direct action between the iron oxide and hydrogen begins, the mass of the chemically active hydrogen is relatively great, and the speed at which the direct action between the hydrogen and the iron oxide commences is considerable; as the direct action progresses hydrogen is continually used up, its active mass becomes continually less, and the speed of the direct action diminishes constantly. In the same way, the reverse action between iron and hydrogen oxide, involving at first a very small mass of hydrogen oxide diffused through a large mass of hydrogen, progresses at first slowly, and then, as the active mass of the hydrogen oxide increases, acquires greater velocity, until finally the direct and the reverse actions are taking place simultaneously at the same rate of speed.

If now we introduce into the system an additional amount of hydrogen, the equilibrium will be disturbed, and the direct action will be set up again and will proceed with continuously diminishing rapidity, until another condition of equilibrium is reached, and a similar effect in setting up the direct action will follow the removal of some of the steam from the system. If, on the other hand, we increase the amount of steam in the system, or remove some of the hydrogen, the effect will be to set up the reverse action, which will proceed with lessening rapidity to another equilibrium.

If we conduct the operation in an open tube, supplying a constant stream of hydrogen to the iron oxide, leading away the steam as fast as it is formed, the direct action, or reduction of iron oxide to iron, may be made to go on continuously to its completion, that is, until the iron oxide is all reduced to iron; and similarly, by supplying a constant current of steam to the iron, and removing the hydrogen as fast as it is formed; we may insure the completion of the reverse action, the oxidation of the iron to iron oxide.

Chemical Equilibrium. *In general a reaction which forms active products retained in the system will result ultimately in a condition of balance or chemical equilibrium between active reagents; while reactions which form products inactive or removed from the sphere of activity as fast as they are formed will continue to completion.*

Reactions in Solution. Reactions which take place through the medium of a solvent, that is between substances of which at least one is in solution, follow also this general rule.

A Reversible Reaction. When magnesium chloride and ammonium hydroxide are brought together in solution, we have evidence of chemical change in the precipitation of magnesium hydroxide; magnesium and "ammonium" have changed places, to some extent at least, with the formation of ammonium chloride and magnesium hydroxide.

Magnesium Chloride + Ammonium Hydroxide
= Ammonium Chloride + Magnesium Hydroxide

The reaction, however, never proceeds to completion, portions of the original magnesium chloride and ammonium hydroxide remaining in the solution. If now we add to the mixture more ammonium chloride, one of the products of the reaction, the reaction is visibly reversed and the magnesium hydroxide begins to be acted upon. When enough ammonium chloride has been added, the magnesium hydroxide all disappears.

Magnesium Hydroxide + Ammonium Chloride
= Ammonium Hydroxide + Magnesium Chloride

This reaction is the exact reverse of that by which the original precipitation takes place. Plainly the reason why the reaction between magnesium chloride and ammonium hydroxide never goes to completion is to be found in the fact that the ammonium chloride and magnesium hydroxide formed tend to interact and reverse the action. The reaction should therefore be expressed as a reversible reaction.

Magnesium Chloride + Ammonium Hydroxide
$\rightleftarrows$ Magnesium Hydroxide + Ammonium Chloride

Completed Reactions. *When, however, one of the products produced by the interaction of substances, of which at least one is in solution, becomes inactive because it is removed from the sphere of action as fast as it is formed, no reversal of the reaction can result.*

Gaseous Product. Thus, when sulphuric acid and sodium carbonate interact in solution, sodium sulphate is formed and remains dissolved, while the gaseous carbon dioxide, coming from the decomposition of the unstable carbonic acid, escapes.

Sodium Carbonate + Sulphuric Acid
= Sodium Sulphate + Carbon Dioxide + Hydrogen Oxide

Since the carbon dioxide is a gas, and therefore spontaneously removable from the sphere of activity, the reaction proceeds to completion. *So it appears that when a reaction takes place between substances, of which at least one is in solution, with formation of a gaseous product removable spontaneously from the system of action, the reaction will proceed to completion.*

Change in Volatility of Product. If we bring into a solution of ammonium chloride a quantity of white, insoluble, freshly precipitated calcium carbonate, the interaction between the two substances is at ordinary temperatures so slight as to be imperceptible; but when, by prolonged boiling of the solution, the ammonium carbonate formed is broken up and the products volatilized, thus being removed from the sphere of activity, the reaction will proceed to completion.

Ammonium Chloride + Calcium Carbonate
= Ammonia Carbonate + Calcium Chloride

So it is sometimes possible to disturb a chemical equilibrium established between substances, of which at least one is in solution, and so complete the reaction, by increasing the volatility of one of the products.

Insoluble Product. When potassium chloride and silver nitrate interact in solution, the potassium changes place with the silver to form insoluble and inactive silver chloride.

Potassium Chloride + Silver Nitrate
= Potassium Nitrate + Silver Chloride

We find by experiment that silver chloride and potassium nitrate are very inactive toward one another, and the reaction of potassium chloride upon silver nitrate is not appreciably reversed by the presence of potassium nitrate. The formation of silver chloride goes on, therefore, until practically all the silver of the silver nitrate or the potassium chloride is exhausted. *So, when one of the products produced by the interaction of substances through the medium of a solvent is insoluble, and at the same* *time inactive, the equilibrium must be continually disturbed, and the reaction will go on to completion.*

Change in Solvent Effect of Medium.

When calcium chloride and potassium sulphate are brought together in solution, the calcium changes place with the potassium, forming calcium sulphate and potassium chloride.

$$\text{Calcium Chloride} + \text{Potassium Sulphate} \rightleftarrows \text{Calcium Sulphate} + \text{Potassium Chloride}$$

Precipitation of the sparingly soluble calcium sulphate may or may not take place, according to the amount of materials and liquid present. In any event, the reaction will be incomplete. When, however, we add to the solution a quantity of alcohol in which calcium sulphate is very insoluble and inactive, we so alter the properties of the medium as to insure the almost complete removal of the calcium sulphate by precipitation in insoluble and inactive form, thus disturbing the equilibrium and permitting the reaction to proceed toward completion. *So it is sometimes possible to disturb a chemical equilibrium between substances at least one of which is in solution, and so insure the progress of the reaction toward completion, by changing the solvent effect of the medium for one of the products formed.*

Product not Hydrolyzed by Water.

In general, the reaction of neutralization between a base and an acid, involving the production of water, proves to be not reversible by water, and proceeds to completion. Thus potassium hydroxide and hydrochloric acid interact in water solution to form soluble potassium chloride and water.

$$\text{Potassium Hydroxide} + \text{Hydrochloric Acid} = \text{Potassium Chloride} + \text{Hydrogen Oxide}$$

The water solution of potassium chloride may be boiled and evaporated to dryness without noticeable reversal of the reaction and the formation of hydrochloric acid.

So, also, when potassium hydroxide and nitric acid interact in water solution, soluble potassium nitrate and water are formed, and, the reaction not being reversible by water under the conditions, proceeds to completion.

$$\text{Potassium Hydroxide} + \text{Nitric Acid} = \text{Potassium Nitrate} + \text{Hydrogen Oxide}$$

Product Hydrolyzed by Water. Reactions of neutralization are, however, not always complete reactions. For example, when arsenious hydroxide and hydriodic acid are brought together in a small amount of water yellow insoluble arsenious iodide is formed.

Arsenious Hydroxide + Hydriodic Acid
= Arsenious Iodide + Hydrogen Oxide

The addition of a suitable amount of water reverses the action and hydrolysis takes place with solution. If now strong sulphuric acid, which as we know possesses a strong affinity for water, is added to the solution, the reverse action of the water is limited and the arsenious iodide is again precipitated.

Similarly, the degree to which hydrochloric acid may be neutralized by arsenious hydroxide depends upon the amount of water present, but the reverse action of water may be limited by adding strong sulphuric acid or strong hydrochloric acid, both of which have a strong attraction for water.

When the mutual neutralization of a base and an acid results in the formation of a product not hydrolyzed by water, the reaction is complete; and when the reaction of neutralization is incomplete because of the formation of a product hydrolyzed by water, it is sometimes possible to push the reaction toward completion by the addition of a substance having a strong attraction for water but otherwise inert under the conditions.

Physical Equilibrium. Many changes in matter — whether physical and of condition merely, or chemical and of composition — are reversible in obedience to small changes in the external conditions of energy represented by temperature and pressure. Water in contact with its own vapor is obviously such a system — since liquid water may be converted to vapor by accession of heat, and, conversely, the vapor thus formed may be condensed again to liquid water by removal of heat. The liquid water and water vapor of the system are said to be in *physical equilibrium.*

Chemical Equilibrium. Similarly, the chemical individual calcium carbonate when heated at a temperature sufficiently high and pressure sufficiently low breaks up into two chemical individuals, calcium oxide and carbon dioxide. Temperature and pressure may, however, be so fixed that no change shall take place in the calcium carbonate under the conditions, while the slightest diminution of pressure or elevation of temperature will set up dissociation of the calcium carbonate into calcium oxide and carbon dioxide. If now under conditions of temperature and pressure at which dissociation takes place, the pressure be slightly increased or the temperature be slightly lowered, the calcium oxide and carbon dioxide combine to form calcium carbonate. The dissociation of the calcium carbonate to the two oxides and the combination of the two oxides to form calcium carbonate constitute a reversible process, and the oxides make a system in *chemical equilibrium.*

The Phase Rule.

In correlating phenomena of equilibrium between substances associated in a reversible process, whether the association is chemical or physical, the thermodynamically deduced "Phase Rule" of Gibbs has proved to be most serviceable.

Phases and Components.

In a material system, those masses of matter which are chemically and physically homogeneous, or of uniform concentration, or which consist of the same mass in the unit volume, and are mechanically separable, are termed "phases," and the substances of independently variable concentration constituting the phases are called "components."

Thus, in the system consisting of calcium oxide, carbon dioxide, and calcium carbonate, the calcium oxide and the carbon dioxide are components, since the amount of each present, both free and combined, is independent of the amount of the other. The amount of the calcium carbonate, however, is dependent upon the amounts of calcium oxide and carbon dioxide present, these substances combining to form calcium carbonate and being formed when calcium carbonate is decomposed. Calcium carbonate, therefore, is not a component, but is to be regarded as a solid phase in which the two components, calcium oxide and carbon dioxide, are associated and, as it happens, in definite proportions.

A component is not necessarily a chemical individual, element, or compound, nor need every chemical individual be regarded as a component. For example, a system made up of propyl alcohol and water in such proportions that the vapor has the same composition as the liquid mixture may be looked upon as consisting of one component (the mixture of definite proportions) and the two phases, liquid and vapor. A hydrous double salt compounded of two salts and water of crystallization is not to be treated as a single component, but rather as three components (two single salts and water), because the concentration of these substances, or masses in the unit volume, may be varied, and by such variations of concentration all possible modifications of the system can be formed.

A system may contain one or more components and may consist of one or more phases. The substance water, for example, makes a system of one component, and the phases may be one, two, or three, according as the water exists as ice, liquid water, or water vapor; or as any two of three phases; or as all three of them.

The effect of changes in temperature, pressure, and concentrations of the phases on equilibrium turns upon the constitution of the system. Assuming values for temperature, pressure, and chemical potentials (the amounts of work involved in the transfer of the unit mass of each component into a phase, or from a phase under defined conditions) to be uniform throughout the system, it has been shown by Gibbs that each phase may be described by an equation connecting these quantities, the same variables appearing in the various equations.

Conditions of Equilibrium.

While we do not know the chemical potentials and are ignorant of the values entering into single equations, *it is possible to draw some conclusions in respect to the conditions of equilibrium of phases as related to temperature, pressure, and concentration.* It appears that when the number of phases is less by one than the number of the components, that the temperature, pressure, and the set of concentrations may vary independently without the disappearance of a phase, the system being variable in three respects, and possessing three *degrees of freedom.* In such a system, as well as in all systems in which the number of phases is less than the number of the components, the possibilities of equilibrium are many and ill defined.

The only systems of practical interest are:

I. *The nonvariant system,* in which the number of phases exceeds the number of the components by two, and which possesses no degree of freedom, it being possible to change neither temperature, pressure, nor concentration without destroying the equilibrium of the phases.

II. *The univariant system,* in which the number of phases exceeds the number of components by one, and which possesses one degree of freedom, it being possible to vary any one of the three determining conditions, temperature, or pressure, or concentration of phase, while the other two assume definite values, without destroying the equilibrium of the phases.

III. *The bivariant system,* in which the number of phases equals the number of components, and which possesses two degrees of freedom, it being possible to vary two of the three determining conditions independently of one another while the third assumes a dependent value, without destroying the equilibrium of the phases.

If C be the number of components, P the number of phases, and F the degrees of freedom, then:

For the nonvariant system . . . $C+2=P+0$
For the univariant system . . . $C+2=P+1$
For the bivariant system . . . . $C+2=P+2$
and, in general, $C+2=P+F$
whence, $P=C+2-F$
and $F=C+2-P$

So it appears, that *the number of phases possible under any conditions is equal to the number of the components increased by two and diminished by the number of degrees of freedom of the system; and, that the number expressing the degrees of freedom of the system is equal to the number of the components increased by two and diminished by the number of phases.*

This relation of components, phases, and degrees of freedom finds useful application in the consideration and classification of various reversible chemical changes.

Degrees of Solubility.

In systems involving the solubilities of components in one another it is plain that concentrations of phase turn upon degrees of solubility. So long as the system involving a soluble salt presents but one set of conditions of equilibrium, — namely, a fixed degree of solubility, one temperature, and one pressure, — it is nonvariant and the number of phases exceeds the number of components by two; when the system shows different degrees of solubility on the part of the dissolved salt with coördinated variations of temperature and pressure, there being for a given temperature only one pressure and one degree of solubility, or for a given pressure one temperature and one solubility, the system is univariant and the number of phases exceeds the number of components by one; and when the system shows changes in solubility corresponding to different temperatures at an assumed pressure, or to different pressures at a fixed temperature, the system is bivariant, and the number of phases is equal to the number of the components. The experimental determination of solubilities under observed conditions of temperature and pressure, and the consequent fixing of the system of equilibrium, may sometimes serve a useful end in discovering new and unexpected compounds.

Now, let us look, for the sake of illustration, at some typical systems of equilibrium, taking first the case of a *system consisting of one component.*

Nonvariant System of One Component.

Water at 0° and 4 mm., the temperature at which ice, liquid water, and water vapor can exist together in equilibrium, is a system of one component, so constituted that its phases can exist in equilibrium at only one temperature, one pressure, and one set of concentrations.

The system is *nonvariant* because the least permanent change of temperature, pressure, or concentration of either ice, liquid water, or water vapor destroys the equilibrium of phases; elevation of temperature melting the ice and causing disappearance of the solid phase, while lowering the temperature freezes the water and removes the liquid phase; increase of pressure condensing the vapor, while decrease of pressure vaporizes the water; and changes of concentration implying, in this case, changes of temperature and pressure.

It is of interest to note, however, that changes of *volume* which do not affect permanently temperature or pressure may be made in such a system without changing the concentration. Suppose, for example, the system of ice, liquid water, and water vapor to be contained in a cylinder closed by a movable piston and at constant temperature and pressure. If the piston is now drawn out, the volume to be filled with vapor is increased, and some water evaporates to fill the space at the given temperature and pressure. Conversely, if the piston is pushed in, the volume to be filled with vapor is diminished and more liquid forms. So long as any water vapor remains, the volume of the system may be varied without changing concentrations or affecting the equilibrium. No permanent change takes place in either event in the concentration of the ice, the liquid water, or the water vapor.

Univariant System of One Component. Liquid water and water vapor existing together at a temperature above that of melting ice constitute a *univariant system*, or a system so made up that for a given combination of phases one and only one of the determining conditions, temperature, pressure, and phase concentration, may be arbitrarily changed without overturning the equilibrium of the phases. There are many temperatures, for each one of which there is a single pressure and a single set of liquid and vapor concentrations for which the phases may be in equilibrium; there are many pressures, for each of which there is a single temperature and a single set of concentrations of equilibrium; and there are many sets of concentration of liquid and vapor, for each of which one temperature and one pressure of equilibrium exists.

The same thing is true in a general way of the univariant system consisting of liquid water and ice, or of ice and water vapor. For each of certain temperatures chosen arbitrarily within limits one pressure and one set of concentrations will be found at which the equilibrium of the phases is preserved. For each of certain arbitrarily chosen pressures there exists a temperature and a set of concentrations at which the equilibrium holds, and for each arbitrarily fixed set of concentrations will be found one temperature and one pressure of equilibrium.

The *volume* of such a univariant system may, however, be changed, providing pressure and temperature are not disturbed, without affecting concentrations. If, for example, the system of liquid water and water vapor be contained in the experimental cylinder at constant temperature and pressure, above 0° and 4 mm., the piston may be drawn out and the volume of vapor expanded so long as liquid water remains, or the piston may be pushed in and the volume of vapor contracted so long as vapor remains, without changing the concentration of either liquid water or water vapor. The conditions are similar for ice and water vapor, at 0° and a pressure less than 4 mm., and the same is true for ice and liquid water, at 0° and a pressure above 4 mm., though possible variations in the volume of this system are very small even under enormous pressures.

Bivariant System of One Component. Water existing as ice, as liquid water, or water vapor makes a *bivariant system* so constituted that two of the determining conditions, temperature, pressure, and phase concentration, may be varied independently. For a given temperature there are many pressures and concentrations, for a given pressure many temperatures and concentrations, and for a given concentration many pressures and temperatures at which ice or liquid water or water vapor may exist without the appearance of another water phase — that is, in equilibrium with itself.

In such a system any change in *volume* implies change in concentration.

Diagrammatic Representation. *The relations of temperature and pressure to equilibrium of the phases in a system of one component may be illustrated by the diagram which we have previously used to illustrate the persistence of phases without discussing questions of equilibrium.* This diagrammatic representation which is here reproduced shows the relations of equilibrium of the three phases of water under varying conditions of temperature and pressure. *The ordinates represent pressures, the abscissæ temperatures, and every point a pressure and a temperature at which at least one phase may exist.* Each curve is made up of points every one of which indicates a pressure and a temperature under which two different phases may coexist, and the point of intersection of the curves indicates a pressure and a temperature at which all three phases may coexist.

Thus the points p_1, p_2, p_3 represent each a pressure and a temperature at which water vapor, liquid water, and ice, respectively, may exist alone. The curve *PA* is made up of points showing the temperatures and pressures at which liquid water and water vapor may exist together in equilibrium; the curve *PB* indicates temperatures and pressures at which the liquid and solid phases of water may be in equilibrium; the curve *PC* shows the equilibrium temperatures and pressures for the solid water phase and water vapor phase.

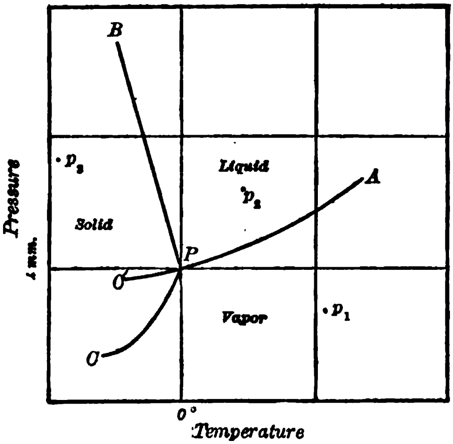


FIG. 34. — Phase Diagram for Water.

Triple Point. This point *P* in which the three curves intersect, called the *triple point*, indicates the one condition of temperature, nearly 0°, and pressure, about 4 mm., at which all the phases of water may coexist. Every point of the curves PA, PB, PC represents the single temperature for every indicated pressure and the single pressure for every indicated temperature at which the univariant systems, vapor-liquid, liquid-solid, and solid-vapor, respectively, may exist. Every line parallel to an axis within the areas APC, APB, BPC, is made up of points representing the several temperatures for every indicated pressure and the several pressures for every indicated temperature at which the bivariant systems of water vapor, liquid water, and solid water, respectively, may exist.

Metastable Phase. *Under exceptional circumstances, the existence of a phase may sometimes be continued when it might ordinarily be expected to disappear.* For example, if pure water is kept perfectly still, it may be cooled below 0° without freezing, though contact with ice may induce immediate solidification. The supercooled water is a phase less stable than ice, and mechanical disturbance converts it to ice; it is said to be the *metastable phase.* The existence of such a metastable phase of water is indicated by the line PC'.

Critical Condition. So also *at a very high temperature no variation of pressure suffices to change the phase of a component.* Water vapor at 370° may be condensed to liquid water by a pressure of 195.5 atmospheres, but above this temperature, — the *critical temperature* of water, — no amount of pressure brings about condensation, and water can exist above 370° in one phase only. The point of critical temperature, 370°, and of *critical pressure,* 195.5 atmospheres, of water, is shown in the diagram by A, the point at which the curve of equilibrium between liquid water and water vapor ends.

System of Two Components. As an example of a *system of two components,* we may consider the case of the solution of sodium chloride, or common salt, in water. The components of the system are two, and the phases may (if we exclude the possibility of a chemical combination of the salt with water) be four, three, or two in number.

Nonvariant System of Two Components. At a temperature sufficiently low, the system made up of the components in proper proportions may consist of solid salt, ice, saturated salt solution, and water vapor. These phases are only in equilibrium at one temperature and one pressure, and the system is *nonvariant.* A permanent change of temperature causes the disappearance of a phase, the solution freezing or the ice melting; a permanent change of pressure liquefies the vapor, or vaporizes the liquid water. In the event of change in either pressure, temperature, or concentration (for no arbitrary change of phase concentration is possible without change of pressure and temperature), the equilibrium of the nonvariant system of four phases disappears and the system becomes *univariant.*

Changes in the *volume* of the nonvariant system which do not affect permanently temperature or pressure may be made, however, as in the nonvariant system of one component, without affecting the concentrations of the phases or overturning the equilibrium. Suppose, for example, the system of solid salt, ice, saturated salt solution, and water vapor to be contained, at a constant temperature and pressure, in the experimental cylinder closed by a movable piston. When the piston is drawn out, the volume to be filled by vapor is increased, and water will evaporate from the solution to fill the space at the given pressure and temperature. As the water is removed, salt will be deposited from the solution, but so long as any liquid water remains, the concentration of the solution, as well as that of the vapor above it and that of the salt deposited from it, will be unchanged. Should all the water be vaporized, the solution phase disappears and the system becomes univariant.

When the piston is pushed in, vapor is condensed and more liquid water dissolves more solid salt, but the concentrations of vapor, solution, and solid remain unchanged so long as any space remains to be filled with vapor. When no more space remains for the vapor, the vapor phase disappears and the system becomes univariant.

There is but one temperature, one pressure, and one set of concentrations at which the nonvariant system exists.

Univariant System of Two Components. If the conditions of temperature, pressure, and phase concentration are such that the system consists of three phases, — solid salt, saturated solution, and water vapor, — the system is *univariant*. In such a univariant system, one of the determining conditions, either the temperature, pressure, or phase concentration, may be varied within limits without disturbing equilibrium between the phases. Thus, when the temperature is raised or lowered, new concentrations are established, notably for the solution by reason of variations in solvent power, and a new pressure must be fixed to counteract the changed vapor tension, but equilibrium may continue if the amount of variation does not go far enough to cause all the salt to dissolve. Variation of pressure implies the fixing of a new temperature to secure the necessary vapor tension to oppose condensation of the vapor and the consequent changes in concentration, notably of the solution, but the equilibrium may be maintained provided some salt remains undissolved. Arbitrary change of concentration can be brought about only by correlated change of temperature and pressure.

Changes of *volume* not involving changes of temperature or pressure may be made within limits without involving changes of concentration. Suppose the system of solid salt, salt solution, and water vapor to be contained in the experimental cylinder closed by a movable piston. At a constant temperature the vapor pressure is constant for a given volume, and so for a given position of the piston. When the piston is drawn out, the volume is increased, and more water will evaporate into the enlarged space. The amount of water in the saturated solution being diminished, some of the dissolved salt will be deposited in the solid phase. So long as there is enough water in the system to supply both liquid and vapor, the equilibrium is preserved between the existing phases, and the concentration of the phases remain the same. When, on the other hand, the volume of the system is diminished, by pushing the piston inward, vapor will condense to form liquid water, more of the solid in contact with the liquid water will dissolve, and less solid salt will remain. The concentrations of each of the phases, however, will remain the same, so long as any space is left for vapor besides that filled by the solid and solution. When no more space is left for vapor, that phase disappears and the system is transformed to a bivariant system. For the univariant system of solid salt, salt solution, and water vapor there is for each of many temperatures one pressure and one set of concentrations, for each of many pressures one temperature and one set of concentrations, and for each of many sets of concentrations one temperature and one pressure at which the equilibrium of the phases may exist.

When variation of volume of the univariant system of solid salt, salt solution, and water vapor is carried so far that for a given temperature the pressure cannot be kept constant by the conversion of more liquid to vapor or of more vapor to liquid, equilibrium can no longer be preserved, a phase will disappear, and the system will become bivariant. Thus, a permanent diminution of pressure below the equilibrium pressure will cause the water of the solution to vaporize until only the solid salt and the water vapor will remain; similarly, an increase of pressure above the equilibrium pressure will condense water vapor until only salt solution and solid salt are left. In like manner, for a given pressure similar effects follow the sufficiently wide variation of temperature, permanent increase of temperature above the equilibrium temperature vaporizing water and compelling the disappearance of the liquid phase until only solid salt and water vapor remain, while decrease of temperature below the equilibrium temperature condenses the vapor phase until only solid salt and salt solution are left.

For the *bivariant systems* of solid salt and salt solution, of solid salt and water vapor, of salt solution and water vapor, there are many temperatures and many sets of concentrations for a given pressure, and many pressures and many sets of concentrations for a given temperature, and many temperatures and many pressures for a given set of concentrations at which equilibrium of the phases may exist. Just as changes in the conditions of pressure, temperature, and concentration of the nonvariant system may result under suitable conditions in the transformation of the nonvariant system to a univariant system, and of the univariant system to a bivariant system, so the reverse changes in the conditions of the system may result in the conversion of a bivariant system to a univariant system, and of the latter to a nonvariant system.

Just as relations of temperature to pressure may be shown diagrammatically by means of coördinates in a plane, so relations of temperature and concentration, or of pressure and concentration, may be illustrated similarly; and since concentrations depend upon solubilities, the relations of temperature or pressure to the solubilities of substances may be indicated similarly. To represent simultaneously relations between the three variables, temperature, pressure, and concentration or solubility, recourse must be had to coördinates in space of three dimensions and the relations of surfaces and solid figures.

CHAPTER XI

HEAT AND THERMAL EQUIVALENTS

In dealing with the heat energy of a substance, or system of substances, we note, on the one hand, the temperature or tendency of the substance or system to exchange heat with other substances, and, on the other hand, the varying capacities of substances to absorb or release heat for definite rises or falls in temperature.

FIG. 35. Mercury Thermometer.

Temperature: the Thermometer.

Temperature changes are measured by the effect of heat upon the volume of a suitably selected material, and ordinarily we use to indicate such changes the *mercury thermometer*, which consists of a capillary glass tube of uniform bore, ending in a bulb which is filled with mercury, and sealed while hot. As the bulb and tube cool, the volume of the mercury diminishes, a vacuous space is left in the tube, and the mercury stands at a point dependent upon the degree of cooling. We may note the point at which the mercury rests when tube and bulb are immersed in a mixture of melting ice and water and call it the 0° of our scale; warming the tube and bulb again, we may fix the point at which the mercury rests when surrounded by steam under a pressure of 760 mm. at the sea level and in latitude 45° and call it 100°; and then if we divide the space between 0° and 100° into one hundred parts, and extend the divisions proportionately below 0° and above 100°, we have a thermometer graduated on the *centigrade scale.*

The Centigrade Scale and the Absolute Scale.

For scientific purposes this is the thermometric scale in ordinary use, but it is plain that the mode of graduation is arbitrary and that we might use any other proportional division of the thermometer stem which seemed to be desirable. We find it of frequent advantage, for example, to make use of another scale upon which 0° centigrade shall be 273°, and 100° centigrade shall be 373°.

This is the *absolute scale*, and it is, as we have seen, very convenient when we have to follow changes of volume of a gas as the temperature changes, because a change of every degree upon this scale corresponds to a change of nearly $\frac{1}{273}$ of the volume of the gas at 273° absolute or at 0° centigrade.

The Common Calorie. As a unit of capacity for heat we may take the amount of heat necessary to raise a given weight of any selected substance through a given interval of temperature. There are several recognized "units of heat," of which the one most convenient for our purpose is the *common calorie*, or the amount of heat necessary to raise by 1° the temperature of 1 grm. of water taken at 18°. Sometimes the water is taken at 0° instead of at 18°, and then the calorie differs from the common calorie by about $\frac{1}{1000}$ of its value.

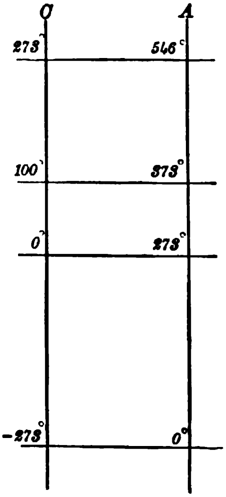


FIG. 36.—Centigrade and Absolute Scales.

Specific Heat. *The quantity of heat required to raise the temperature of 1 gram of a substance 1°, stated in terms of the quantity of heat required to raise the temperature of 1 gram of water 1° at 18°, is the specific heat of the substance.*

Specific Heats of Solid Elements. A study of the *specific heats of the elementary substances* brings out an interesting relationship between the specific heats and the chemical equivalents of the elements. Dulong and Petit showed, in 1819, that *the product obtained by multiplying the specific heats of certain solid elements by their common chemical equivalents is an approximately constant quantity, 6; and that in the case of some other elements the product of the specific heat by a simple multiple or fraction of the common equivalent is approximately the same constant quantity, 6.* In spite of the obstacles in the way of very exact determinations of specific heats, such as difficulties in manipulation and in the preparation of pure materials, and the fact that specific heats are somewhat variable with the physical condition of the elements, the rule of Dulong and Petit has been extended by many investigators, among whom Regnault was prominent, to include a large number of the elements, provided the specific heats are determined for the element in solid form and at a temperature not too near the melting point.

The specific heats of the elements in the gaseous condition and in the liquid condition, excepting mercury, do not, so far as they have been examined, follow the rule of Dulong and Petit; and four solid elements of low equivalent weight, glucinum, boron, carbon, silicon, which show unusually variable specific heats as the temperature rises, follow the rule even approximately only at high temperatures. That the ordinarily gaseous elements, hydrogen, nitrogen, oxygen, chlorine, should not come within the rule of Dulong and Petit is not surprising, since we know that change of phase involves great change in the specific heat, water, for example, at 18° having a specific heat which we make 1 common calorie, while the specific heat of ice is 0.502 common calories, and that of steam is 0.37 common calories.

Specific Heats and Chemical Equivalents of Elements.

If we let E stand for the equivalent of an element, n for a simple number or fraction, and h for the specific heat of the element, then

$$nEh = 6 \text{ (approximately)}.$$

Thus for magnesium, which has a specific heat of 0.250 common calories and an equivalent of 24.36 we have

$$nEh = 1 \times 24.36 \times 0.250 = 6.09$$

and similar results follow for other elements.

Chemical Equivalents and Specific Heats

Element	Simple Number or Fraction		Chemical Equivalent		Specific Heat Com. Cal.		Product
	n	×	E	×	h	=	6 (approx.)
Carbon, at 978°	2	×	6.00	×	0.463	=	5.56
	1	×	12.00	×	0.463	=	5.56
Copper	1	×	63.6	×	0.095	=	6.04
	½	×	127.2	×	0.095	=	6.04
Iodine	1	×	126.97	×	0.054	=	6.88
Iron	1	×	55.9	×	0.112	=	6.26
Lead	1	×	206.9	×	0.031	=	6.42
Magnesium	1	×	24.36	×	0.250	=	6.09
Mercury	1	×	200.0	×	0.032	=	6.40
Platinum	1	×	194.8	×	0.032	=	6.23
Potassium	½	×	78.30	×	0.166	=	6.50
Sodium	½	×	46.10	×	0.293	=	6.75
Sulphur	1	×	32.06	×	0.178	=	5.71
Zinc	1	×	65.4	×	0.093	=	6.08

Now, reversing the procedure, and dividing the approximate average, 6, by the specific heats of the elements, numbers may be obtained which represent weights of approximately equal heat capacity, and these weights prove to be nearly identical with the common chemical equivalents, or with simple multiples or fractions of the common chemical equivalents. It is not unreasonable to suppose that the weights of equal heat capacity are the common chemical equivalents, or simple fractions or multiples of the common chemical equivalents.

Thermal Equivalents of Elements.

If we make this supposition and then call weights of equal heat capacity *thermal equivalents*, we may say that *the thermal equivalent of an element is either the common chemical equivalent, or else that simple fraction or multiple of the common chemical equivalent which approximates most closely to the number obtained by dividing 6 by the specific heat of the solid element.*

Following we have a list of the thermal equivalents thus derived from the preceding table:

THERMAL EQUIVALENTS

(Weights of Equal Heat Capacity)

Carbon	12.00	Mercury	200.0
Copper	63.6	Platinum	194.8
Iodine	126.97	Potassium	39.15
Iron	55.9	Sodium	23.05
Lead	206.9	Sulphur	32.06
Magnesium	24.36	Zinc	65.4

This relation of the thermal equivalents to the chemical equivalents brings up the idea suggested in the law of multiple proportions, that the common chemical equivalents of the elements may in reality be made up of individual masses of the elements taken in simple aggregations. This is a point to which we shall recur.

Specific Heats of Compounds.

It appears upon investigation of the *specific heats of compounds* that in many cases the specific heat of a solid compound is determined by the heat capacities of the component elements; and that the product of the equivalent into the specific heat when divided by the number of thermal equivalents approximates the number 6. For example, lead iodide, consisting of 44.896 per cent.

of lead and 55.104 per cent. of iodine, has a specific heat of 0.0427 com. cal. The number 206 9 represents the thermal equivalent, as well as the chemical equivalent, of lead; so the amount of iodine combined with one equivalent of lead in lead iodide is found by the proportion:

$$44.896 : 55.104 = 206.9 : x \quad (x = 253.94)$$

The number 253.94 represents the equivalents, chemical and thermal, of iodine; so lead iodide must be put together in proportions corresponding to 1 equivalent of lead, 206.9, to 2 equivalents of iodine, 253.94, or three in all, and making 460.84 the equivalent of the compound.

Now $$460.84 \times 0.0427 = 19.68$$

and $$\frac{19.68}{3} = 6.56$$

the average constant for each equivalent represented.

Obviously this relation of the specific heat of a compound to the specific heats of its components makes it possible to determine the number of thermal equivalents composing the compound, and so to get a figure for the thermal equivalent of any constituent in the compound. Thus, in lead iodide, 206.9 represents 1 equivalent of lead, and 253.94 represents n equivalents of iodine, in the equivalent of the compound, 460.84. Then, the specific heat of lead iodide being 0.427 com. cal.,

$$460.84 \times 0.0427 = 19.68$$

and $$\frac{19.68}{6} = 3+$$

the number of equivalents.

There are, therefore, three equivalents in the compound, of which the number 206.9 represents 1 equivalent of lead, while 460.84 — 206.9, or 253.94 represents 2 equivalents of iodine. So 126.97 must be the thermal equivalent of iodine, and this corresponds to the thermal equivalent fixed directly by the specific heat of solid iodine.

For lead chloride, composed of 74.477 per cent. of lead and 25.523 per cent. of chlorine, an element of unknown thermal equivalent, the specific heat is found to be 0.0644 com. cal. By the proportion,

$$74.477 : 25.523 = 206.9 : x \quad (x = 70.90)$$

we find the weight, 70.90, of chlorine which is associated with one equivalent of lead, 206.9, in the equivalent of the compound, 277.80.

Now $$277.80 \times 0.0644 = 17.89$$

and $$\frac{17.89}{6} = 3-$$

the number of equivalents.

So it appears that in an equivalent of lead chloride there are three equivalents of the elements lead and chlorine, of which one is lead. The number 70.90 must stand for two equivalents of chlorine, and the thermal equivalent of chlorine in the compound is 35.45.

The thermal equivalents of other elements may be studied similarly. Experiment has shown, however, that those elements which, when free, do not follow the rule of Dulong and Petit, do not generally obey the rule when in combination. Thus the compounds of glucinum, boron, carbon, and silicon give in combination low values for the specific heats, as they do in free condition unless the temperature is very high. The gaseous elements, hydrogen, nitrogen, oxygen, are likewise irregular in behavior and both free and combined are exceptions to the rule.

We shall have occasion to return soon to a consideration of the thermal equivalents in their relation to electrical equivalents and chemical equivalents.

Heat Changes in Reactions.

The heat changes involved in chemical reactions may be determined and expressed in common calories. Substances react, as we know, in equivalent proportions, and in dealing with weighed amounts of material we find it convenient to speak of the quantities in grams which are proportional to the equivalents as *gram-equivalents*. Thus, 2.015 grm. of hydrogen and 16 grm. of oxygen and 18.015 grm. of water are a gram-equivalent of hydrogen, a gram-equivalent of oxygen, and a gram-equivalent of water, respectively. When a gram-equivalent of hydrogen combines with a gram-equivalent of oxygen to produce a gram-equivalent of water, heat is evolved. The exact amount liberated depends to some extent upon the physical condition of the water formed. If the water formed remains gaseous, the amount of heat evolved is different from that set free if the water is condensed to liquid, since in the condensation latent heat is liberated. When a gram-equivalent of hydrogen and a gram-equivalent of oxygen are taken at 18°, and the water formed is condensed to the liquid condition at 18°, the heat evolved amounts to 68,360 common calories; while that evolved when hydrogen and oxygen at 100° form gaseous water at 100° amounts to 58,000 common calories.

Gram-equivalents.

These conditions may be expressed by the equations:

Hydrogen +	Oxygen	= Liquid Water	+ *68,360 com. cal.*
1 grm.-equiv.	1 grm.-equiv.	1 grm.-equiv.	
Hydrogen +	Oxygen	= Gaseous Water	+ *58,000 com. cal.*
1 grm.-equiv.	1 grm.-equiv.	1 grm.-equiv.	

To reproduce the elements hydrogen and oxygen from water it is necessary to add from without 58,000 common calories of heat for every gram-equivalent of gaseous water decomposed, and 68,360 common calories of heat for every gram-equivalent of liquid water decomposed.

Heat of Formation of Compounds. *The heat effect noted when a compound is formed from its elements in definite physical condition is known as the heat of formation of the substance for that condition; and in the process by which the elements are again separated an exactly equivalent heat effect is observed, but in the opposite direction.* This was shown to be the case by Lavoisier and Laplace.

Heat Effect of Reactions. Hess was the first to point out, in 1840, that *the thermal effect of a reaction depends solely on the initial state and final state of the system* and not at all upon the intermediate stages. This is a principle of importance in the interpretation of the heats of hydration of acids, bases, and salts, and the heats of formation of many compounds.

Let us, for example, determine the heat of formation of calcium chloride in the action of calcium oxide upon a dilute solution of hydrochloric acid to form a dilute solution of calcium chloride in water.

Calcium Oxide +	Hydrogen Chloride =	Calcium Chloride +	Water +	*46,230 com. cal.*
	(dilute solution)	(dilute solution)		
1 grm.-equiv.	1 grm.-equiv.	1 grm.-equiv.	1 grm.-equiv.	
56.10 grm.	72.915 grm.	111 grm.	18.015 grm.	

Now let us take the reaction in stages, first forming calcium hydroxide, then dissolving it in water, then neutralizing the solution with dilute hydrochloric acid to get the dilute solution of calcium chloride in water.

(1)	Calcium Oxide	+ Water =	Calcium Hydroxide	+ *15,540 com. cal.*
	1 grm.-equiv.	1 grm.-equiv.	1 grm.-equiv.	
(2)	Calcium Hydroxide	+ Water =	Calcium Hydroxide Solution	+ *2,790 com. cal.*
	1 grm.-equiv.	*n* grm.-equiv.		
(3)	Calcium Hydroxide Solution +		Hydrogen Chloride	
			1 grm.-equiv.	
	= Calcium Chloride +		Water	+ *27,900 com. cal.*
	1 grm.-equiv.		1 + *n* grm.-equiv.	
				Total, 46,230 com. cal.

Obviously the summation of the effects of the intermediate reactions gives us the effect of proceeding at once from the initial stage to the final stage.

Exothermic and Endothermic Reactions and Compounds.

We find it useful to distinguish between reactions in which heat is evolved and reactions in which heat is absorbed. *Reactions in which heat is evolved are called exothermic reactions, and reactions in which heat is absorbed are called endothermic reactions.* The combination of hydrogen with oxygen is an exothermic reaction, while the decomposition of water into hydrogen and oxygen is an endothermic reaction.

Hydrogen	+	Oxygen	=	Hydrogen Oxide	+	*68,360 com. cal.*
1 grm.-equiv.		1 grm.-equiv.		1 grm.-equiv.		
Hydrogen Oxide	=	Hydrogen	+	Oxygen	–	*68,360 com. cal.*
1 grm.-equiv.		1 grm.-equiv.		1 grm.-equiv.		

Compounds which are formed from elementary substances with evolution of heat are called exothermic compounds, while compounds formed from elementary substances with absorption of heat are termed endothermic compounds. Water is an exothermic compound; acetylene gas proves to be an endothermic compound.

Sometimes reactions are at once set up when substances are brought into contact, as when hydrogen chloride and ammonia gas meet under ordinary atmospheric conditions. Generally energy must be supplied from outside the system to start a reaction, but in any event the reaction once started may proceed exothermically or endothermically according to conditions. Thus, hydrogen and oxygen when mixed in proportions to form water remain inactive until a temperature of 200° is reached; between 200° and 1000° the reaction proceeds exothermically in the sense of the equation:

Hydrogen + Oxygen = Hydrogen Oxide

Above 1000° the reverse reaction sets in:

Hydrogen Oxide = Hydrogen + Oxygen

At 2500° both reactions are proceeding equally; and at still higher temperatures the endothermic separation of water into its elements predominates. On cooling, the reaction proceeds exothermically more and more until the temperature is reached at which water is the sole product. In general, endothermic compounds produced at high heat tend to act exothermically as the temperature falls and so to separate into their constituents. In acetylene, which may be produced from its elements, carbon and hydrogen, at the extremely high temperature of the electric arc, we have an example of an endothermic substance stable at high temperatures and less stable at lower temperatures. At ordinary temperatures endothermic bodies are not easily produced unless the total effect of the reaction producing them is exothermic, or unless the energy is supplied from outside in the form of electricity.

Energy Relations. Exothermic compounds are usually more stable at the lower temperatures, and it appears to be true that chemical reactions which proceed at ordinary temperatures without accession of outside energy are generally, but not always, exothermic. Thus, ordinary combustions are exothermic reactions, and so are the neutralization processes which occur spontaneously between acids and bases. It appears to be true that chemical reactions tend toward the running down of energy in the system, but that energy may disappear by conversion to an unavailable form as well as by liberation in the form of heat; and it frequently happens that reactions take place endothermically, that is, in the direction not indicated by the maximum evolution of heat. It may, however, be said that *most chemical changes proceed in the direction of the maximum disengagement of heat*— a condition which was formerly made imperative by both Thomson and Berthelot for all purely chemical changes.

The relation between heat energy and electrical energy is a matter of interest. The physicists are able to determine the mechanical equivalents of heat and electricity, and we are in position to know that the electricity applied in separating electrolytically a gram-equivalent of matter, oxygen being taken as 16, does for every volt of potential required an amount of work equivalent to 46,000 common calories. So, leaving out of consideration incidental and secondary expenditures of energy, *we may find the potential of current necessary to decompose a substance by dividing by 46,000 the heat of formation, expressed in common calories, of one gram-equivalent of the substance.* The following table shows the heats of formation of gram-equivalents of some of the common oxides, and the voltage of electricity necessary to bring about the decomposition of the oxides:

HEAT OF FORMATION AND ELECTRICAL POTENTIAL OF DECOMPOSITION OF OXIDES

OXIDE	HEAT OF FORMATION	ELECTRICAL POTENTIAL OF DECOMPOSITION
1 Gram-equivalent	Common Calories	Volts
Sodium Oxide (62.1 grm.)	99,760	2.17
Calcium Oxide (56.1 grm.)	130,930	2.84
Zinc Oxide (81.4 grm.)	85,430	1.85
Copper Oxide (79.6 grm.)	37,160	0.81
Hydrogen Oxide (18.015 grm.) . . .	68,360	1.48

The Water Calorimeter. A convenient apparatus for measuring quantity of heat is the *water calorimeter*, a simple form of which is shown in the figure. A platinum vessel, *A*, of about 600 cm.^{3} capacity, rests upon pieces of cork within a thin copper vessel, *B*, which is, in turn, supported upon corks within a silver vessel, *D*, fitted to a double-walled sheet-iron vessel, *C*, filled with water, to act as a heat screen, and covered with felt. All this elaborate precaution is taken to keep heat from entering the innermost vessel of platinum or from escaping from it unregistered. In the platinum vessel, fitted with a thermometer and stirrer, is put a known weight of water whose changing temperature is to be noted. Upon the introduction of a substance of different and known temperature, or of substances

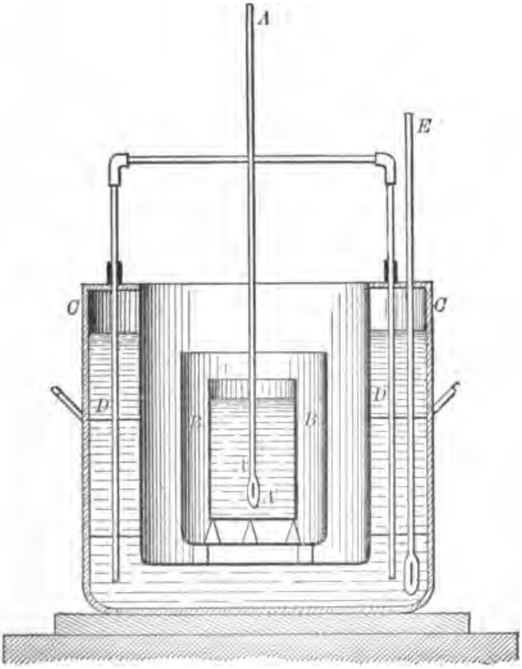


FIG. 37.—Water Calorimeter.

which by their reaction upon one another or upon the water produce thermal change, the thermometer shows the change in temperature of a known weight of water, and so the number of calories communicated to the water and to the platinum vessel may be calculated. Corrections must, of course, be made for the heat capacity of the platinum vessel, and for many sources of error included in the "constant of the apparatus," determined by careful experiment. Such an apparatus finds use in determining the heat changes involved in the solution of substances, in the neutralization of acids and bases, or in other reactions in solution.

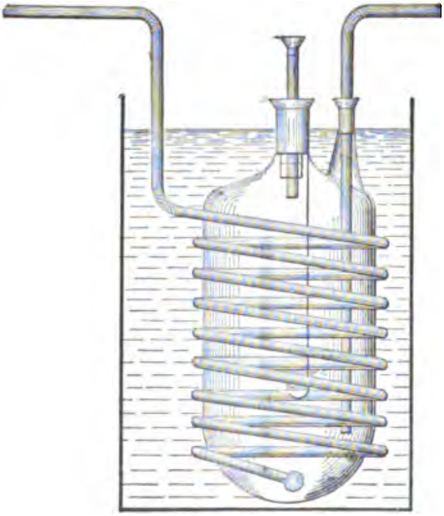


FIG. 38. — Combustion Chamber.

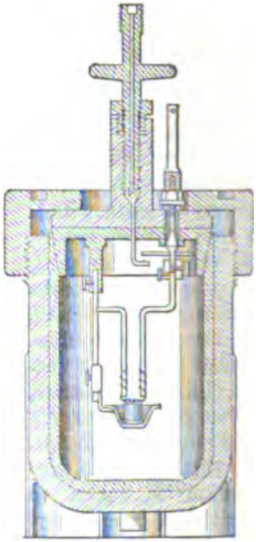


FIG. 39. — Explosion Bomb.

Combustion Chamber.

When the heat evolved in the combustion of substances is to be found, a little chamber in which definite weights of material are burned may be kept within the calorimeter during the entire process. The figure shows a little *combustion chamber*, thus arranged for burning sulphur. In most of the recent work upon heats of combustion the *explosion bomb* of Berthelot has been used. In this apparatus, a sketch of which is shown, combustion of the substance under examination is brought about in compressed oxygen, and ignition is made by electricity, the whole bomb being submerged in the water chamber of a suitable calorimeter. Obviously, many corrections must be found by experiment and applied in order that the true deductions may be made

Explosion Bomb.

from the observed rise in the temperature of the calorimeter. We are in possession of much valuable information gained by this apparatus.

Ice Calorimeter. Another form of calorimeter, especially adapted to the handling of small amounts of material, is the *ice calorimeter* of Bunsen, in which the quantity of heat communicated is measured by the amount of ice melted to water, and determined by the contraction of a mass of ice and water. This calorimeter consists of a test-tube, *T*, sealed into a bulb, *S*, to which is fused a capillary graduated tube. Water and mercury are introduced by judicious manipulation, with heating and cooling, until they occupy the relative position shown in this figure. By running through the test-tube a current of alcohol cooled below 0°, ice may be frozen in the bulb. After removing the alcohol and replacing it by a little water the apparatus is placed in a vessel filled with snow to prevent accession of outside heat, and after standing some time, the whole, mercury, water, ice, attains a temperature of 0°, and the mercury stands at a constant level in the capillary tube. Any melting of the ice about the test-tube must change the volume of ice and water in the bulb and cause proportional movement of the mercury in the tube. To determine the heat liberated by a known weight of a substance when cooled through a given range of temperature, it is only necessary to heat the substance to a definite temperature, as for example to 100° in a test-tube placed in a current of steam, and then to drop the substance as quickly as may be into the test-tube of the calorimeter. The substance gives heat to the water and is cooled to 0°, the water passes on the heat to the ice and water in the bulb, being itself thereby cooled to 0°, and the whole apparatus assumes the original temperature, the only change being the melting of ice at 0° to water at 0°, and the consequent definite change of volume corresponding to the definite addition of heat.

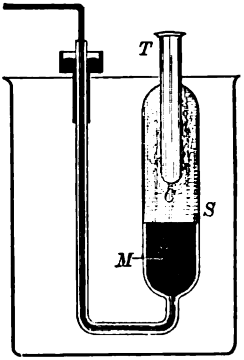


FIG. 40. — Ice Calorimeter.

It is plain that different quantities of heat transmitted from the water in the test-tube to the ice and water in the bulb are brought into comparison when the movements of the mercury in the capillary tube are noted. Very small quantities of material may be handled in this way, and to Bunsen and his pupils we owe the determination of the amounts of heat liberated from definite small quantities of rare materials when cooled from 100° to 0°. Inasmuch as a substance loses as much heat when cooled through a definite interval of temperature as it takes up when heated through the same interval of temperature, these calorimetric determinations show the relative capacities of substances for taking up heat through definite rise of temperature.

CHAPTER XII

CHEMICAL MASS-UNITS AND SYMBOLS

Equivalents of Oxygen.

In our study of the composition of the series of nitrogen oxides, it was shown that when the weights of nitrogen are taken as fixed at 28.08 throughout the series, the weights of oxygen appear as 16 and simple multiples of 16, the number which we have taken as the fixed equivalent of oxygen. Thus, in the series of five nitrogen oxides, we have successively combined with 28.08 parts by weight of nitrogen 1 × 16, 2 × 16, 3 × 16, 4 × 16, and 5 × 16 parts by weight of oxygen respectively, these numbers representing 1, 2, 3, 4, 5 equivalents of oxygen respectively, combined with 1 equivalent of nitrogen taken as 28.08.

EQUIVALENTS OF OXYGEN IN NITROGEN OXIDES

NITROGEN OXIDE	NITROGEN	OXYGEN
Nitrogen monoxide	28.08 (1)	16.00 (1 × 16.00)
Nitrogen dioxide	28.08 (1)	32.00 (2 × 16.00)
Nitrogen trioxide	28.08 (1)	48.00 (3 × 16.00)
Nitrogen tetroxide	28.08 (1)	64.00 (4 × 16.00)
Nitrogen pentoxide	28.08 (1)	80.00 (5 × 16.00)

Individual Masses and Equivalents of Oxygen.

Now, if we assume, as has been previously suggested, that oxygen enters into its compounds in individual masses which have a definite and invariable weight, and that nitrogen also enters into its compounds in individual masses of another definite and invariable weight, then these peculiar numerical relations seem to be natural, since *the proportions by weight of oxygen and nitrogen in the nitrogen oxides now appear to be due to the aggregation in varying numbers of individual masses of these elements.*

Thus, if we take the equivalent of oxygen, 16, as the weight of the individual mass of oxygen, and the equivalent of nitrogen in nitrogen monoxide, 28.08, as the weight of the individual mass of nitrogen, then it appears that any given weight of nitrogen monoxide must be made up of individual masses of nitrogen and individual masses of oxygen combined in definite equal numbers, or in the proportion 1 : 1; that any given weight of nitrogen dioxide must be made up of definite numbers of individual masses of nitrogen and individual masses of oxygen combined in the proportion 1 : 2; and that given weights of nitrogen trioxide, nitrogen tetroxide, and nitrogen pentoxide must be made up of individual masses of nitrogen and individual masses of oxygen combined in definite numbers in the proportions 1 : 3, 1 : 4, and 1 : 5, respectively.

Or, should we prefer to take the number 14.04, one half the equivalent of nitrogen in nitrogen monoxide, to represent the weight of the individual mass of nitrogen relative to the individual mass of oxygen taken as 16, we should have another series of proportions, namely, 2 : 1, 2 : 2, 2 : 3, 2 : 4, 2 : 5, to represent the relative numbers of individual masses of nitrogen and oxygen in combination in equal given weights of the nitrogen oxides.

Individual Masses of Elements in Combination.

In either event the numbers 1, 2, 3, 4, 5, representing simple multiples of the weight of the individual mass of oxygen which appear throughout the series for the same weight of nitrogen, express the proportionate numbers of individual masses of oxygen which are in combination with the same number of individual masses of nitrogen in the nitrogen oxides. In the combination of individual masses of nitrogen with individual masses of oxygen in definite numbers, we may find explanation of the numerical relations of the equivalents of nitrogen and oxygen found in the nitrogen oxides. In general, *the relations of the equivalents of elements entering into combination may be explained upon the assumption that the elements enter into compounds in individual masses which act as units in chemical action.*

The Thermal Equivalent and the Mass-unit.

Now let us recall our experience with electrical equivalents and thermal equivalents in their relation to chemical equivalents. Since the electrical equivalent of an element, fixed by Faraday's Law, is identical with the chemical equivalent, and like the chemical equivalent is different in many compounds and reactions, the electrical equivalent throws no further light on the relations of the individual masses. On the other hand, *the thermal equivalents of all elements which come within the rule of Dulong and Petit appear to be invariable, whether the elements are free or combined, and to represent masses of the elements of equal heat capacity.* This fact suggests that the thermal equivalents of the elements, representing masses of matter of definite heat capacity, may very reasonably be taken to be aggregations in equal numbers of the individual masses which acts as units in chemical action. *We may, therefore, reasonably take the thermal equivalent of an element to represent the weight of the individual mass of the element,* by the assumption of which we find explanation for the definite composition of individual compounds, and for the simple numerical relations of the equivalents of elements in combination. So we may arrange a series of numbers, each of which, with the exception of a very few, represents at the same time the invariable thermal equivalent and the weight of the individual mass, or, as we may for convenience call it, the *mass-unit* of the element, in terms of the equivalent of oxygen, assumed to be the mass-unit of oxygen, taken as 16. *For oxygen, nitrogen, and hydrogen, which are gaseous elements, and do not follow the rule of Dulong and Petit, we shall assume arbitrarily that the equivalents 16, 14.04, and 1.0075 represent respectively weights of the mass-units.* In subsequent study of the compounds into which these elements enter, we shall find this assumption to be justified.

With the adoption of the idea of the mass-unit of the element, the equivalent of an element or compound appears to represent an aggregation of mass-units of the same kind or of different kinds in definite number. *The mass-unit weight of an element is a simple equivalent of the element, and the simple equivalent of a compound is that particular equivalent which is expressed by the simplest aggregation of mass-units.*

Mass-unit Weight.

Mass-unit Symbols.

If, therefore, we take convenient characters to represent single mass-units of the elements, it is clear that *the composition of any individual compound may be represented by the combination of characters for the individual mass-units making up the simple equivalent of the compound.*

For the symbol of a single mass-unit of an element it is usual to take the initial letter of the English name of the element, or two letters selected from the name in case the initial letter has been previously appropriated to indicate some other element, or one or two letters taken from the Latin name.

In the following table are given the accepted symbols of the mass-units of some common elements, with their mass-unit weights, the mass-unit weight of the oxygen being taken as 16:

MASS-UNITS OF ELEMENTS

ELEMENT	SYMBOL OF MASS-UNIT	WEIGHT OF MASS-UNIT
Bismuth	Bi	208.5
Calcium	Ca	40.1
Carbon	C	12.00
Chlorine	Cl	35.45
Copper (Cuprum)	Cu	63.6
Hydrogen	H	1.0075
Iodine	I	126.97
Iron (Ferrum)	Fe	55.9
Lead (Plumbum)	Pb	206.9
Magnesium	Mg	24.36
Mercury (Hydrargyrum)	Hg	200.0
Nitrogen	N	14.04
Oxygen	O	16.00
Potassium (Kalium)	K	39.15
Silver (Argentum)	Ag	107.93
Sodium (Natrium)	Na	23.05
Sulphur	S	32.06
Zinc	Zn	65.4

Equivalent Symbols of Compounds. When we know the proportionate composition of any compound, as determined by analysis, and the mass-unit weights of the constituent elements, it is easy to find the proportionate numbers of the mass-units which will express in the simplest way the proportionate composition of the simple equivalent, and so to make the "equivalent symbol" of the compound. Thus, we know by analysis that 100 parts by weight of water contain 11.18 parts by weight of hydrogen and 88.82 parts by weight of oxygen. We know, also, that the mass-unit of hydrogen weighs 1.0075 and the mass-unit of oxygen 16. Our problem is to find the simple ratio of numbers of mass-units which will express the composition of water. Obviously, the ratio of these numbers will be the ratio of the quotients 11.18 ÷ 1.0075 and 88.82 ÷ 16, or 11.10 : 5.55. These numbers stand in the simple ratio of 2 : 1, so the equivalent symbol of water will be made up of 2 mass-units of hydrogen and 1 mass-unit of oxygen.

The equivalent symbol of water will be HHO, and expressing the repetition of the mass-unit symbol by a figure placed to the right and below that symbol, we have H_2O for the equivalent symbol of water.

Similarly, since carbon dioxide consists of 72.73 parts by weight of oxygen, and 27.27 parts by weight of carbon, and the mass-unit weights of oxygen and carbon are 16 and 12 respectively, we find that CO_2 is the equivalent symbol of carbon dioxide.

In general, *we may make the equivalent symbol of a compound by dividing the percentage proportions of the individual constituents given in the analysis of the compound by the weights of the mass-units of the respective constituents, and writing the whole numbers which express most simply the ratio of these quotients against the respective mass-unit symbols placed together.* We frequently speak of the equivalent symbol as simply the symbol of the compound.

The equivalent symbol of a compound indicates:

(1) The constituent elements of the compound;

(2) The number of mass-units of each kind which make up the simplest equivalent;

(3) The proportionate composition by weight of the simple equivalent, the mass-unit weight of oxygen being taken as 16;

(4) The proportionate composition by weight of the compound in any system of units, *e.g.* the percentage composition.

Thus, we have found for water the equivalent symbol H_2O, from which we may extract exactly the information which we utilized in making the symbol, — that water consists of hydrogen and oxygen; that 2 mass-units of hydrogen and 1 mass-unit of oxygen make up the simple equivalent; that the simple equivalent consists of 2.015 parts by weight of hydrogen to every 16 parts by weight of oxygen; and that water consists of 11.18 per cent. of hydrogen and 88.82 per cent. of oxygen.

Equivalent symbols of some of the compounds which we have studied are given in the table:

EQUIVALENT SYMBOLS OF COMPOUNDS

Bismuth trioxide	Bi_2O_3
Calcium oxide	CaO
Carbon dioxide	CO_2
Copper oxide	CuO
Hydrogen oxide	H_2O
Mercury oxide	HgO
Nitrogen monoxide	N_2O
Nitrogen dioxide	NO
Nitrogen trioxide	N_2O_3
Nitrogen tetroxide	NO_2
Nitrogen pentoxide	N_2O_5
Zinc oxide	ZnO
Calcium hydroxide	$Ca(OH)_2$
Potassium hydroxide	KOH
Sodium hydroxide	$NaOH$
Zinc hydroxide	$Zn(OH)_2$
Hydrogen chloride	HCl
Potassium chloride	KCl
Sodium chloride	$NaCl$
Zinc chloride	$ZnCl_2$
Bismuth nitrate	$Bi(NO_3)_3$
Bismuth hydroxyl nitrate	$Bi(OH)(NO_3)_2$
Nitric acid	HNO_3
Potassium nitrate	KNO_3
Sodium nitrate	$NaNO_3$
Sulphuric acid	H_2SO_4
Magnesium sulphate	$MgSO_4$
Potassium sulphate	K_2SO_4
Potassium hydrogen sulphate	$KHSO_4$
Calcium carbonate	$CaCO_3$

By the use of equivalent symbols, problems relating to composition by weight of the substances represented are easily solved.

Calculations from Equivalent Symbols. In the equivalent symbol for the hydrated crystallized copper sulphate, $CuSO_4 \cdot 5H_2O$, for example, the equivalents of the various constituents, taken in relation to the sum of all the equivalents, represent the *proportionate composition* of crystallized copper sulphate.

$$\begin{array}{ll} Cu & = 63.60 \\ S & = 32.06 \\ O_4(4 \times 16.00) & = 64.00 \\ 5\,H_2O(5 \times 18.015) & = \underline{90.07} \\ CuSO_4 . 5\,H_2O & = 249.73 \end{array}$$

Thus we know that 249.73 parts by weight of crystallized copper sulphate contain 63.60 parts of copper, 32.06 parts of sulphur, 64.00 parts of oxygen, and 90.07 parts of water. The numbers thus obtained from the equivalent symbol may be converted to percentages by solving the following equations, the results of which represent the *percentage composition* of crystallized copper sulphate:

$$\begin{array}{ll} 249.73 : 63.60 = 100.00 : x, & (x = 25.47, \text{ copper}) \\ 249.73 : 32.06 = 100.00 : y, & (y = 12.84, \text{ sulphur}) \\ 249.73 : 64.00 = 100.00 : z, & (z = 25.63, \text{ oxygen}) \\ 249.73 : 90.07 = 100.00 : w, & (w = \underline{36.06}, \text{ water}) \\ & (100.00, \text{ copper sulphate}) \end{array}$$

Thus we know that crystallized copper sulphate is composed of 25.47 per cent. copper, 12.84 per cent. sulphur, 25.63 per cent. oxygen, and 36.06 per cent. water.

The weight of any constituent contained in a given weight of crystallized copper sulphate may likewise be found. Suppose, for example, we wish to find the weight of copper, sulphur, oxygen, and water contained in 8 grm. of crystallized copper sulphate. We solve the equations:

$$\begin{array}{ll}
249.73 : 63.60 = 8.00 : x, & (x = 2.04, \text{ copper}) \\
249.73 : 32.06 = 8.00 : y, & (y = 1.03, \text{ sulphur}) \\
249.73 : 64.00 = 8.00 : z, & (z = 2.05, \text{ oxygen}) \\
249.73 : 90.07 = 8.00 : w, & (w = \underline{2.88}, \text{ water}) \\
 & \quad (8.00, \text{ copper sulphate})
\end{array}$$

The figures thus obtained show that 8 grm. of crystallized copper sulphate contain 2.04 grm. of copper, 1.03 grm. of sulphur, 2.05 grm. of oxygen, and 2.88 grm. of water.

The weight of crystallized copper sulphate which will contain a given weight of any constituent is likewise determinable. Thus if we wish to know how much crystallized copper sulphate might be made from 25 grm. of copper we should solve the equation:

$$63.60 : 249.73 = 25.00 : x, \quad (x = 98.16)$$

from which we find that 98.16 grm. of crystallized copper sulphate may be made from 25.00 grm. of copper.

Or, we may find the weight of any constituent of the crystallized copper sulphate when that of any other constituent is known. The weight of sulphur that would be present with 10 grm. of copper in crystallized copper sulphate would be found from the equation:

$$63.60 : 32.06 = 10.00 : x, \quad (x = 5.04)$$

from which we find that 5.04 grm. of sulphur are present with 10 grm. of copper in crystallized copper sulphate.

From the equivalent symbol of a compound, therefore, we may calculate:

(1) *The proportionate composition of the substance in any system of units, as in percentages;*

(2) *The weight of any of the constituents contained in a given weight of the substance;*

(3) *The weight of the substance containing a given weight of any constituent;*

(4) *The weight of any constituent which is associated with a given weight of any other constituent.*

We have at various times found it convenient to represent chemical changes by equations. *Inasmuch as in chemical changes we are dealing*

Equations of Equivalent Symbols.

with the reactions of equivalents, it is possible to represent the factors and products of a reaction by their equivalent symbols. Thus, in the decomposition of water, hydrogen and oxygen are the sole products, and it is easy to so arrange the statement in symbols that the equivalent of water composed of mass-units of hydrogen and oxygen shall appear as a factor, while the products, hydrogen and oxygen, shall be represented by their individual mass-units. Thus, the equation

$$H_2O = 2H + O$$

indicates:

(1) That water decomposes into hydrogen and oxygen;

(2) That the simple equivalent of water produces two mass-units of hydrogen and one mass-unit of oxygen;

(3) That 18.015 parts by weight of water decompose to form 2.015 parts by weight of hydrogen, and 16 parts by weight of oxygen.

It is obvious that in an equation made up of symbols the same number of mass-units of each kind must appear on both sides of the equation, and that total weights of the mass-units of each kind involved in any equation represent the relative weights of the corresponding substances, stated in any system of weights.

Calculations from Equations of Equivalent Symbols.

From the equation representing a chemical change we may, therefore, determine the weight of a given substance, or part of a substance, present either as a factor or as a product, when we know the weight of any other represented substance or part of a substance, either factor or product.

Thus, let us suppose that we want to know the weight of hydrogen which may be produced by the decomposition of 10 grm. of water. Writing in the equation, which represents the chemical change, the equivalent symbol of water, and the mass-unit symbols of hydrogen, at the same time indicating the simple equivalent weight of water with the mass-unit weights of hydrogen, and introducing in their proper places the weight of the substance given and the x to represent the weight of the substance called for, we have

$$\begin{array}{cccccc} H_2O & = & 2H & + & O \\ 18.015 & & 2.015 & & \\ 10 \text{ grm.} & & x \text{ grm.} & & \end{array}$$

whence, $18.015 : 2.015 = 10 : x, \quad (x = 1.12)$

We find that 1.12 grm. of hydrogen are set free from 10 grm. of water.

Furthermore, since the volume of a substance may be deduced from its weight when the weight of any given volume is known, and since our tables of specific gravities give us the experimental determinations of the weights of given volumes of substances with reference to the weights of the same volumes of certain standard substances under defined conditions, it follows that *from an equation representing a chemical change we may determine the volume of any substance taking part in the change when we know the specific gravity of the substance and the weight of any other substance taking part in the change.*

Let us suppose that we want to know, in the first place, how many cubic centimeters of water reduced to standard condition, 4°, may be obtained by heating 10 grm. of crystallized copper sulphate. For the equation and statement of the problem, we have:

$$\begin{array}{lcl} CuSO_4 \cdot 5H_2O & = CuSO_4 + & 5H_2O \\ 249.73 & & 90.07 \\ 10.\ \text{grm.} & & x\ \text{grm.} \\ & & y\ \text{cm.}^3 \end{array}$$

Solving the problem first as to weight, we have

$$249.73 : 90.07 = 10 : x, \quad (x = 3.61)$$

whence it appears that from 10 grm. of crystallized copper sulphate we get 3.61 grm. of water.

Now, 1 grm. of water at 4° just fills 1 cm.^{3}; so 3.61 grm. of water will have a volume of 3.61 cm.^{3} at 4°.

Let us suppose we want to know what the volume of the water will be at 0°, still liquid; at 100° as liquid water; at 0° converted to ice; and at 100° as steam. These are all problems of practical interest. Turning to the table which we made when we were studying the properties of water, we find the necessary data.

SPECIFIC GRAVITIES OF WATER

Liquid at 4°	1.00000
Liquid at 0°	0.99987
Liquid at 100°	0.95863
Solid at 0°	0.91730
Gaseous at 100°	0.00059

These figures give the relative weights of equal volumes of water under the different conditions, as compared with the weight of the same volume of water at 4°, and, of course, the weights of 1 cm.^{3} of water under the different conditions in terms of the weight of 1 cm.^{3} of water at 4°; but 1 grm. of water at 4° fills 1 cm.^{3}, and *these figures for specific gravity therefore express the weights in grams of 1 cm.^{3} of water under the different conditions.*

So, if we divide the weight in grams of the water obtained from our problem by these figures, expressing the specific gravities, we shall have the volume of the water under the different conditions.

The 3.61 grm. of water would occupy:

$$\frac{3.61}{1} = 3.61 \text{ cm.}^3 \text{ at } 4^\circ \text{ in the liquid phase;}$$

$$\frac{3.61}{0.99987} = 3.6104 \text{ cm.}^3 \text{ at } 0^\circ \text{ in the liquid phase;}$$

$$\frac{3.61}{0.95863} = 3.77 \text{ cm.}^3 \text{ at } 100^\circ \text{ in the liquid phase;}$$

$$\frac{3.61}{0.9173} = 3.93 \text{ cm.}^3 \text{ at } 0^\circ \text{ in the solid phase;}$$

$$\frac{3.61}{0.00059} = 6119 \text{ cm.}^3 \text{ at } 100^\circ \text{ in the gaseous phase.}$$

We have found, therefore, that the water derived from 10 grm. of crystallized copper sulphate would occupy: in liquid form, 3.61 cm.^{3} at 4°, 3.6104 cm.^{3} at 0°, 3.77 cm.^{3} at 100°; as ice, 3.92 cm.^{3} at 0°; and as steam, 6120 cm.^{3} at 100°.

Calculation of Volumes from Weights. In general, *the volume of a substance in cubic centimeters may be found by dividing the weight of the substance in grams by the specific gravity of the substance referred to water at 4°.*

$$V \text{ (in cm.}^3\text{)} = \frac{W \text{ (in grm.)}}{\text{Specific Gravity (to Water at } 4^\circ\text{)}}$$

Specific Volume. Moreover, if we know the *specific volume* of a substance, that is, the reciprocal of the specific gravity, or the volume of the substance which has the same weight as one cubic centimeter of a standard substance under defined conditions, we may use that instead of the specific gravity in our calculations. So, *the volume of a substance in cubic centimeters may also be found by multiplying the weight of the substance in grams by the specific volume of the substance referred to water at 4°.*

$$V \text{ (in cm.}^3\text{)} = W \text{ (in grm.)} \times \text{Specific Volume (to Water at } 4^\circ\text{)}$$

Standards of Specific Gravity. The specific gravities of solids and liquids are generally referred to water at 4°. For gaseous substances it is more convenient to select some standard gas, to the weight of a given volume of which the weights of the same volume of other gases may be referred. Hydrogen, the lightest of the gases, is often taken as a standard; sometimes it is convenient to use air, which is a mixture of nearly constant composition; and quite recently *it has become customary to refer the specific gravities of gases to an ideal gas, a given volume of which is assumed to have $\frac{1}{32}$ of the weight of the same volume of oxygen.* The specific gravity of a gas is

The Ideal Gas.

sometimes spoken of as *gas density*, and the gas density of a substance which ordinarily exists as a solid or liquid is sometimes spoken of as the *vapor density* of the substance.

We have already defined the specific gravity of a substance as the weight of a unit volume of the substance in terms of the weight of the unit volume of a standard substance taken under standard conditions.

$$\text{Or, Specific gravity} = \frac{\text{Weight 1 unit volume}}{\text{Weight 1 unit volume standard under standard conditions}}$$

Solids and Liquids. For *solids* and *liquids* the unit volume is 1 cm.^{3}, while the standard substance is *water*, and the standard condition is that of the greatest concentration of water, *4°*. One cm.^{3} of water at 4° weighs 1 grm. *The specific gravity of a solid or of a liquid referred to water may be found by dividing the weight of 1 cm.^{3} of the solid or liquid at 4° by the weight of 1 cm.^{3} of water at 4°, or in other words, by 1.*

$$\text{Specific gravity to water at } 4^\circ = \frac{\text{Weight 1 cm.}^3\text{ solid or liquid}}{\text{Weight 1 cm.}^3\text{ water (1)}}$$

Since solids and liquids change their volumes slightly with changing temperature, their specific gravities vary somewhat at different temperatures. We may say, however, that *under ordinary atmospheric conditions the specific gravity of a solid or a liquid referred to water is expressed by very nearly the same figures that stand for the weight in grams of 1 cm.^{3} of the solid or liquid.*

Gases. In actually weighing substances so light as *gases* it is convenient to adopt a larger volume for comparison, while the readiness with which gases change volume with changing temperatures and pressure requires that conditions of temperature and pressure be defined with great exactness. For gases, then, the unit volume is usually *1 liter*, equal to 1000 cm.^{3}, and the standard substance may be either *hydrogen*, or *air*, or more preferably the *ideal gas*, 1 liter of which is assumed to weigh $\frac{1}{32}$ of the weight of 1 liter of oxygen under similar conditions, *the standard conditions being 0° and a pressure of 760 mm. in latitude 45° at the sea level.* Under standard conditions, 1 liter of hydrogen weighs 0.0899 grm., 1 liter of air weighs 1.2930 grm., while the weight of 1 liter of the ideal gas, equal to $\frac{1}{32}$ of the weight of 1 liter of oxygen, would equal 0.04466 grm. We may say, therefore, that *the specific gravity of a gas is found by dividing the weight of 1 liter of the gas by the weight under standard conditions of 1 liter of hydrogen (0.0899 grm.), 1 liter of air (1.2930 grm.), or 1 liter of the ideal gas (0.04466 grm.), according to which of these standards is selected.*

$$\text{(1) Specific gravity to hydrogen} = \frac{\text{Weight of 1 liter of gas}}{\text{Weight of 1 liter hydrogen (0.0899 grm.)}}$$

$$\text{(2) Specific gravity to air} = \frac{\text{Weight of 1 liter of gas}}{\text{Weight of 1 liter air (1.2930 grm.)}}$$

$$\text{(3) Specific gravity to oxygen/32} = \frac{\text{Weight of 1 liter of gas}}{\text{Weight of 1 liter ideal gas (0.04466 grm.)}}$$

$$\text{(4) Specific gravity to water} = \frac{\text{Weight of 1 liter of gas}}{\text{Weight of 1 liter of water at } 4^{\circ} \text{ (1000 grm.)}}$$

The figures expressing the specific gravity of a gas in terms of any one of the standards may be readily changed to terms of another standard. Thus, we have

$$\text{Specific gravity to hydrogen} \left\{ \begin{array}{ll} = \text{Specific gravity to air} & \times \dfrac{1.2930}{0.0899} \\ = \text{Specific gravity to oxygen/32} & \times \dfrac{0.04466}{0.0899} \\ = \text{Specific gravity to water} & \times \dfrac{1000}{0.0899} \end{array} \right.$$

from which, when the specific gravity of a substance referred to any one of the given standards is known, the specific gravity referred to any other of the given standards may be found.

The weights in grams of 1 liter of each of the gases mentioned, with the approximate specific gravity of each referred to the given standards, are shown in the table:

SPECIFIC GRAVITIES OF GASES

GAS	WEIGHT OF ONE LITER (Under standard conditions) Grams	SP. GR TO OXYGEN/32	SP. GR. TO HYDROGEN	SP. GR. TO AIR	SP. GR. TO WATER AT 4°
Oxygen/32 . . .	0.0446	1.000	0.497	0.0345	0.0000446
Hydrogen . . .	0.0899	2.013	1.000	0.0695	0.0000899
Air	1.2930	28.950	14.400	1.0000	0.0012930
Oxygen	1.4291	32.000	15.900	1.1050	0.0014291
Nitrogen	1.2507	28.020	13.910	0.9670	0.0012507
Chlorine	3.1670	71.010	35.230	2.4500	0.0031670
Hydrogen oxide .	0.8040	18.020	8.930	0.6220	0.0008040
Ammonia. . . .	0.7630	17.110	8.490	0.5900	0.0007630
Hydrogen chloride	1.6285	36.460	18.100	1.2600	0.0016285

In the approximate determinations of the specific gravities of gases we may take advantage of the characteristics of an ideal gas as expressed by the gas laws of Boyle and Charles.

Boyle's Law.

According to Boyle's Law, the volume of any gas is inversely proportional to the pressure put upon it, the temperature remaining constant, as expressed in the proportion:

$$v : v' = p' : p$$

or,

$$vp = v'p' = \text{Constant}$$

Thus, if we should take 1 liter of gas at 760 mm. pressure (1 atmosphere) and double its pressure, the volume would become $\frac{1}{2}$ of 1 liter, while in case we should reduce the pressure to 380 mm. ($\frac{1}{2}$ atmosphere) the gas would occupy 2 liters, provided in each case the temperature of the gas remained constant. These relations were discovered by Robert Boyle, who experimented with a volume of air confined over mercury in a bent tube, closed at one end, so arranged that the compression of the air by successive additions of mercury could be measured on a scale. Boyle published his results in 1660.

Charles' Law.

According to Charles' Law, under constant pressure the volume of a gas varies directly as its absolute temperature, as expressed in the proportion:

$$v : v' = T : T'$$

or,

$$v : v' = t + 273^\circ : t' + 273^\circ$$

Thus, if we should take 273 cm.^{3} of gas at 0° under atmospheric pressure and heat it to 10°, it would expand to 283 cm.^{3}, while at — 10° it would occupy 263 cm.^{3} At 273° it would have doubled its volume, occupying 546 cm.^{3}. These relations were discovered by Charles, and were published by Gay-Lussac in 1802.

We note, therefore, from the experimental study of gases, that *all gases while at constant temperature, expand or contract approximately equal amounts as the pressure put upon them is decreased or increased, respectively;* and that *under constant pressure the same rise and fall of temperature produces in all gases approximately the same increase or decrease, respectively, in volume;* or, in other words, that *all gases have the same coefficient of expansion for heat.*

The Gas Law Equation.

We may regard that gas as an *ideal gas* which follows the gas laws exactly. While no gases are found to answer this requirement perfectly, hydrogen and certain other gases not readily liquefied are found ordinarily to be in very nearly ideal condition. We shall find it convenient to express in a single *gas law equation* the relations of the pressure, absolute temperature, and volume of an ideal gas.

The change in volume of the ideal gas for each degree of change of temperature above or below 0° is $\frac{1}{273}$, or 0.00367, of the volume of the gas at 0°: the *coefficient of expansion of the ideal gas is $\frac{1}{273}$, or 0.00367.*

Hence, if v_0 and v_t stand for the volumes of the gas at 0° and at t° respectively, and if

$$\alpha = \tfrac{1}{273}, \text{ or } 0.00367$$

then,

$$v_t = v_0 (1 + \alpha t)$$

If the temperature be raised without allowing the gas to expand, the pressure changes according to the expression

$$p_t = p_0 (1 + \alpha t)$$

in which p_t is the pressure at the temperature t° and p_0 the pressure at 0°.

The expression,

$$v = v_0 (1 + \alpha t)$$

gives the volume v of a gas at t° and under a constant normal pressure p_0, as $v_0(1 + \alpha t)$. If the pressure be reduced to 1 cm. of mercury, the volume will be increased according to Boyle's Law, so that for the new volume v we have

$$v_0 (1 + \alpha t) : v = 1 : p_0$$

and

$$v = v_0 (1 + \alpha t) p_0$$

If now the gas is compressed by the pressure p, the volume will change according to the expression,

$$v_0 (1 + \alpha t) p : v = p : 1$$

and

$$pv = p_0 v_0 (1 + \alpha t)$$

But T° Absolute = $t° + 273°$, and $t° = T° - 273$. Introducing this value into the equation, we have

$$pv = p_0 v_0 \left[1 + \frac{1}{273}(T - 273)\right] = p_0 v_0 \left(1 + \frac{T}{273} - 1\right)$$

$$= p_0 v_0 \frac{T}{273} = \frac{p_0 v_0}{273} T$$

For a given mass of gas the value $\frac{p_0 v_0}{273}$ is a constant quantity. If we represent this constant by R, we get the *gas law equation*,

$$pv = RT$$

the numerical value of R depending upon the unit of volume and unit of pressure chosen.

Now, if we wish to determine the specific gravity of a gas, we may observe its weight in grams g and its volume v in cubic centimeters at any convenient pressure p in millimeters of mercury, and any convenient temperature t on the centigrade scale. We have then the data necessary to calculate what the specific gravity or gas density of the substance would be with reference to hydrogen, or to air, or to the ideal gas oxygen /32, if both gases could be directly compared at 0°, 760 mm., latitude 45°.

Since $pv = p_0v_0 (1 + at)$, the volume of the gas at 0° and 760 mm. will be given by the expression,

$$v_0 = \frac{pv}{p_0 (1 + at)}$$

The same volume of ideal gas at 0° and 760 mm. will weigh

$$0.0000446 \times \frac{pv}{p_0 (1 + at)}$$

since 1 cm.^{3} of it weighs 0.0000446 grm., whence

$$\text{Specific gravity to oxygen } /32 = g \div \left[0.0000446 \frac{pv}{p_0 (1 + at)} \right]$$

$$= \frac{g (1 + at) p_0}{0.0000446 \, pv}$$

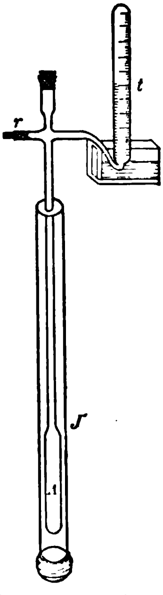


FIG. 41. — Victor Meyer's Displacement Apparatus.

Experimental Determination of Specific Gravities. *It may be well to consider briefly the experimental determination of specific gravities.* To determine the specific gravity of a gas it is only necessary to know the weight of a flask of known capacity filled with the gas at known temperature and pressure, and the weight of the vacuous flask. If v is the known volume of the flask, t the temperature, p the pressure under which the flask is filled, a the weight of the flask filled with gas, and b the weight of the vacuous flask, then v, t, p are known, and $g = a - b$. So we have the data for determining the specific gravity to the ideal gas oxygen /32 according to the formula given above.

Displacement Apparatus. For determining the specific gravity of vapors, substances which exist in the gaseous state only at higher temperatures, many devices have been employed. Of these the *Displacement Apparatus of Victor Meyer* is now most widely used. This device consists of a bulb and tube, *Ar*, heated by appropriate means within the receptacle, *J*. When the temperature of the apparatus is constant and no air issues from it, the measuring cylinder, *t*, is put in place, the tube is opened and into it a weighed amount, *g*, of the substance to be gasified is dropped, the tube being immediately closed. As the substance becomes gaseous near the bottom of the bulb, *A*, a volume of air equal to that of the newly formed gas is displaced. This air collects in *t* and may be measured at the atmospheric temperature and pressure. In accordance with the gas laws the volume, v, noted at the temperature, $t°$, and the atmospheric pressure, p, is the same as that of the gasified substance would be if it could be cooled without condensing to the observed temperature and pressure. So, having g, v, t, and p, the calculation of the specific gravity may be made by the formula given.

Picnometer. For finding the *specific gravities of solids and liquids* a flask closed by a bored stopper, known as a *picnometer*, is convenient. If the weight, a, of the empty apparatus is first found, and then the weight, b, of the apparatus filled with water to the scratch on the bored stopper, at the standard temperature determined once for all, it is only necessary to find c, the weight of the apparatus similarly filled with another liquid, in order that we may have the data for calculating the specific gravity of that liquid. Thus,

$b - a$ = Weight of the volume of water which fills the picnometer,
$c - a$ = Weight of the volume of liquid which fills the picnometer;

whence,

$$\text{Specific gravity of liquid to water} = \frac{c - a}{b - a}$$

The same apparatus serves to determine the specific gravity of solid substances. If g is the weight of the substance, b the weight of the picnometer filled with water, and c the weight of the picnometer with the solid in it and filled for the rest with water, then $b + g - c$ = weight of water displaced from the picnometer, equal in volume to the volume of the solid substance. Whence,

$$\text{Specific gravity of solid to water} = \frac{g}{b + g - c}$$

CHAPTER XIII

MOLECULES

Simple Gram-equivalent.

We have seen that substances which react chemically act in fixed and definite proportions by weight, and that such actions may be interpreted as the reactions of simple equivalents made up of the simplest possible number of elementary mass-units, and may be represented by simple equivalent symbols. In regard to gaseous substances, in particular, we have learned that, in accordance with the Law of Gay-Lussac, the volumes of gases involved in a chemical reaction as factors or products bear to one another the relation of simple whole numbers. It would seem, therefore, that some simple relation must exist between the simple whole numbers which express the relations of volume according to which substances interact and the volume occupied by simple equivalents of the gaseous substances. We have found it convenient to make use of the term *gram-equivalent* to indicate that weight in grams of a substance which is expressed numerically by the equivalent of the substance, and the weight in grams of a substance which corresponds to the simple equivalent, or that equivalent composed of the simplest possible number of elementary mass-units, we may now call the *simple gram-equivalent.* Our problem is, therefore, to see what relation may exist between the simple gram-equivalents of gaseous substances and the volumes which they occupy.

The greater number of such elements as obey, in free condition or in compounds, the rule of Dulong and Petit, and whose mass-units are therefore established, and the greater number of the compounds of such elements, cannot be volatilized without decomposition; but certain of such elements and some compounds, notably certain fluorides, chlorides, bromides, and iodides, may be obtained in gaseous condition, and for such substances we may calculate, from the observed specific gravities, what volumes the simple gram-equivalents would occupy, if reduced in accordance with the gas laws to standard conditions of temperature and pressure.

Thus we have for carbon disulphide 76.12 as the simple equivalent and 76.4 as the observed specific gravity in terms of oxygen/32, and we know that 1 liter of the ideal gas, oxygen/32, weighs 0.0446 grm., under standard conditions. We have, then, for the volume occupied under standard conditions by the simple gram-equivalent, 76.12 grm. of gaseous carbon disulphide,

$$76.12 \div (76.4 \times 0.0446) = 22.34 \text{ liters}$$

In the following table are shown the equivalent symbols, simple gram-equivalents, observed specific gravities to oxygen/32, and calculated volumes occupied by 1 simple gram-equivalent of a number of substances in gaseous condition:

VOLUMES OF SIMPLE GRAM-EQUIVALENTS OF GASEOUS SUBSTANCES

SUBSTANCE IN GASEOUS CONDITION	EQUIVALENT SYMBOL	SIMPLE GRAM-EQUIVALENT Grams	SPECIFIC GRAVITY Oxygen/32 (Determined)	VOLUME OF SIMPLE GRAM-EQUIVALENT Liters
Zinc	Zn	65.40	65.5	22.39
Mercury	Hg	200.00	200.3	22.39
Carbon disulphide .	CS_2	76.12	76.4	22.34
Boron trifluoride . .	BF_3	68.00	66.8	22.82
Silicon tetrafluoride .	SiF_4	104.40	103.3	22.66
Lead chloride . .	$PbCl_2$	277.80	274.9	22.66
Tin dichloride . .	$SnCl_2$	189.90	186.6	22.82
Mercuric chloride . .	$HgCl_2$	270.90	283.5	21.43
Zinc chloride . .	$ZnCl_2$	136.30	133.1	22.96
Antimony trichloride .	$SbCl_3$	226.55	225.5	22.52
Arsenic trichloride .	$AsCl_3$	181.35	182.3	22.30
Bismuth trichloride .	$BiCl_3$	314.85	325.5	21.69
Boron trichloride . .	BCl_3	117.35	116.3	22.62
Phosphorus trichloride .	PCl_3	137.35	141.1	21.83
Carbon tetrachloride .	CCl_4	153.80	153.3	22.50
Silicon tetrachloride .	$SiCl_4$	170.20	171.8	22.21
Tin tetrachloride . .	$SnCl_4$	260.80	266.1	21.97
Mercuric bromide .	$HgBr_2$	359.92	357.8	22.55
Boron tribromide . .	BBr_3	250.88	254.0	22.15
Mercuric iodide . .	HgI_2	453.94	468.7	22.00
Arsenic triiodide . .	AsI_3	455.91	465.8	22.24
Phosphorus triiodide .	PI_3	411.91	418.3	22.38
Silicon tetraiodide .	SiI_4	536.28	552.6	22.05

From these figures we discover at once the very remarkable fact that for these substances in the condition of approximately ideal gases, which obey the gas laws of Boyle and Charles with approximate exactness, the numbers representing the specific gravities, calculated according to the gas laws for standard conditions and referred to oxygen/32, are approximately identical with the numbers which represent the simple equivalents; and calculating the volume which would be occupied under standard conditions by a simple gram-equivalent of each of these gaseous substances, it is found that this volume is approximately the same for all, and is not far from 22.4 liters. It follows from the gas laws that equal volumes of these substances, when in gaseous condition, contain at any fixed temperature and pressure proportionate parts of the simple gram-equivalents of the respective substances; and recalling that the simple equivalents represent for the elements the weights of the mass-units and for compounds the weights of individual aggregations of mass-units, we may say that *equal volumes of these gaseous substances, elementary or compound, contain approximately equal numbers of simple equivalents of the substances.*

Molecules. In the case of the gaseous substances which we have studied, the simple equivalents are apparently the individual masses which are involved in the physical relations of pressure, temperature, and volume; they are the physical units, the masses in which the physical properties of the substances are inherent, as well as the equivalents in chemical action. It is such considerations as these which led Avogadro, in 1811, to say that *the smallest individual mass in which the properties of the substance inheres is the "molecule,"* and to formulate the hypothesis that *in equal volumes of all ideal gases, elements or compounds, there are, under the same conditions of temperature and pressure, the same numbers of molecules.*

Molecular Weights. As a matter of fact, the application of the gas laws is not absolutely exact for any known gas. Hydrogen, oxygen, and nitrogen obey the gas laws very closely, and for most gases at temperatures moderately removed from the points of liquefaction the deviations from the gas laws are small. For the substances of the table the relative weights of the molecules, or *molecular weights*, are indicated only approximately by the specific gravities to oxygen/32, and these are approximately the same as the simple equivalents which are determinable with a higher degree of accuracy. It is evident that *we may* *represent molecular weights by the same system of units by which we express equivalent weights, and we may take, for these substances, the simple equivalents as the molecular weights.*

Variation in Specific Gravity.

As we extend our study of the relations of the equivalents and molecular weights, we occasionally find substances which appear to possess specific gravities gradually changing through certain ranges of temperature, but of definite and persistent value through each of certain considerable ranges of temperature. These specific gravities which are constant for considerable variations in temperature therefore represent definite molecular conditions corresponding to the different ranges of temperature. Thus at temperatures above 760° aluminium chloride has a specific gravity to oxygen/32 of about 133; as the temperature falls the specific gravity undergoes gradual change, while between 440° and 218° the value of the specific gravity to oxygen/32 is nearly constant at about 266. Through each of two definite ranges of temperature from 760° upward, and between 218° and 440°, the molecular weight is constant. At the high range of temperature the specific gravity approximates to the simple equivalent 133.45, corresponding to the symbol $AlCl_3$, and that weight and that symbol must be taken to represent the molecule of aluminium chloride for the higher temperatures; and at the lower range of temperature the specific gravity doubles and the molecule is twice as heavy, and for this molecular weight we take twice the simple equivalent, or 266.90, making the symbol Al_2Cl_6. A similar state of affairs exists as to ferric chloride, $FeCl_3$ and Fe_2Cl_6, and some other compounds.

Molecular Weights of Gases.

In general, to fix the molecular weight of a gaseous substance, we must take that equivalent of the substance to which the specific gravity, referred to oxygen/32, approximates for a considerable range of temperature.

Dissociation of Compounds.

In this way we may find molecular weights for any individual substances which do not undergo chemical decomposition or "dissociation" at the temperature of the experiment. For a substance which gradually dissociates, like ammonium chloride at high temperature,

$$NH_4Cl = NH_3 + HCl$$

the specific gravity cannot be a guide to the molecular weight of the substance, since the specific gravity represents new substances and new molecules which are formed in indeterminate degree in the reaction.

Having found means for determining the molecular weights of gaseous substances, it will be interesting to inquire into the *molecular complexity of these elements which may exist in gaseous condition*, to see whether the molecule of every element consists of a single mass-unit, or whether elementary molecules may be compounded of more than one mass-unit of the same kind.

Molecular Weights of Elements.

To find the approximate molecular weights of an element it will only be necessary to determine the specific gravity to oxygen/32 of the element in gaseous condition; to determine the number of mass-units in the molecule we have only to divide the approximate molecular weight by the mass-unit weight of the element; and, then, to fix the exact molecular weight we may take that multiple of the mass-unit weight of the elements which approximates most closely to the approximate molecular weight, or in other words to the specific gravity to oxygen/32.

In this manner the data of the following table have been determined:

MOLECULAR WEIGHTS OF ELEMENTS

ELEMENT	MASS-UNIT SYMBOL	SPECIFIC GRAVITY (Oxygen/32)	MASS-UNIT WEIGHT	NUMBER OF MASS-UNITS IN MOLECULE	MOLECULAR WEIGHT	MOLECULAR SYMBOL
Hydrogen	H	2.0126	1.0075	2	2.015	H_2
Nitrogen	N	28.00	14.04	2	28.08	N_2
Oxygen	O	32.00	16.00	2	32.00	O_2
		48.00	16.00	3	48.00	O_3
Chlorine	Cl	70.9	35.45	2	70.90	Cl_2
Bromine	Br	159.9	79.96	2	159.92	Br_2
Iodine	I	254	126.97	2	253.94	I_2 (up to 600°)
		127	126.97	1	126.97	I (at 1500°)
Phosphorus	P	124	31.0	4	124.0	P_4 (less than red heat)
Arsenic	As	300	75.0	4	300.0	As_4
		150	75.0	2	150.0	As_2 (at 1700°, white heat)
Sulphur	S	220	32.06	8	220	S_8, S_6
		64	32.06	2	64.12	S_2 (at 1000°)

MOLECULAR WEIGHTS OF ELEMENTS (*Continued*)

ELEMENT	MASS-UNIT SYMBOL	SPECIFIC GRAVITY (Oxygen/32)	MASS-UNIT WEIGHT	NUMBER OF MASS-UNITS IN MOLECULE	MOLECULAR WEIGHT	MOLECULAR SYMBOL
Zinc	Zn	65	65.4	1	65.4	Zn
Cadmium	Cd	112	112.4	1	112.4	Cd
Mercury	Hg	200.3	200.0	1	200.0	Hg
Antimony	Sb	240	120.2	2	240.4	Sb_2

So it becomes evident that in the case of many elements the molecular weights in the gaseous condition prove to be approximately twice the mass-unit weights; in a few cases the molecular weights and the mass-unit weights are identical; while in still other cases the molecular weights are three, four, and even more times as great as the mass-unit weights; and for a few elements the molecular weights in the gaseous condition are found to be different at different temperatures. Some solid elements, such as bismuth, copper, iron, lead, magnesium, manganese, potassium, silver, and sodium, do not volatilize easily enough to permit of the determination of the specific gravities and molecular weights in the gaseous condition. For some elements like carbon and silicon we have thus far been unable to determine the weights of the gaseous molecules.

Composition of Molecules of Compounds.

The figures of analysis of a compound obviously likewise express the proportionate composition of the molecule of the compound. Having the proportionate composition of a compound and knowing its approximate molecular weight, it is an easy matter to find the numbers which express the approximate weight, in terms of oxygen, taken as 16, of any constituent element of the molecule. We may find, for example, what weights of oxygen appear in the molecules of compounds of that element. To make the calculations we have only to form and solve the proportion:

$$100 : \text{per cent. of oxygen} = \text{approximate molecular weight} : x$$

In the table are given the approximate weights of oxygen in approximate molecular weights of compounds of that element, with the necessary data for the calculation:

PROPORTIONS OF OXYGEN IN MOLECULES OF OXYGEN COMPOUNDS

OXYGEN COMPOUND	PER CENT. OF OXYGEN	APPROXIMATE MOLECULAR WEIGHT Specific Gravity to Oxygen/32	APPROXIMATE WEIGHT OF OXYGEN IN THE MOLECULE	
Hydrogen oxide	88.82	18.02	16.005	16
Carbon monoxide	57.14	27.96	15.98	
Alcohol	34.78	46.56	16.23	
Carbon dioxide	72.73	44.14	32.10	32
Sulphur dioxide	49.95	64.90	32.42	
Acetic acid	53.33	60.14	32.07	
Sulphur trioxide	59.95	86.08	51.00	48
Methyl borate	46.15	103.60	47.81	
Ethyl borate	32.88	148.40	48.79	
Ethyl silicate	30.71	210.00	64.49	64

Mass-unit Weight of Oxygen. Obviously the weights of oxygen found in the molecules of these substances approximate to 16 or multiples of 16, the slight variation from these numbers being explained by the fact that we have been dealing only with approximate molecular weights, and so could not expect more than approximate accuracy in the results deduced from these data. Assuming that these slight variations are inaccuracies, *no compound of oxygen is known in the molecule of which the weight of oxygen present is less than the mass-unit weight 16.* So the choice of 16, the common equivalent of oxygen, as the weight of the mass-unit of oxygen, is now justified.

We find, similarly, when we study the compounds of hydrogen and nitrogen, that the mass-unit weights of these elements, arbitrarily chosen, were taken correctly as 1.0075 and 14.04 respectively, these numbers being the smallest amounts of hydrogen and nitrogen ever found in any molecule.

The mass-unit weights of the other elements, fixed by the thermal equivalents, prove likewise to be the smallest weights of these elements which enter into molecules of their compounds.

Molecular Symbols of Elements. When the molecular weight of a gaseous substance is known, it is desirable to express this information in the symbol of the substance, and thus to make a molecular symbol. The *molecular symbol of an element* is made by putting together as many mass-unit symbols of the element as are necessary to express the number of mass-units contained in the approximate molecular weight, which is expressed by the specific gravity referred to oxygen/32. Such a molecular symbol of an element indicates the element, a molecule of the element, the number of mass-units in the molecule, the sum of mass-unit weights, or the molecular weight, and the ideal specific gravity referred to oxygen/32. Thus H_2 indicates hydrogen, a molecule of hydrogen, 2 mass-units of hydrogen, a molecular weight of 2.015, and an ideal specific gravity of 2.015 to oxygen/32.

Molecular Symbols of Compounds. To determine the *molecular symbol of a compound*, we need only the proportionate composition of the compound as given by analysis, and the specific gravity of the compound referred to oxygen/32, which is also the approximate molecular weight. The proportionate composition of the compound expresses also the proportionate composition of the molecules of which the compound consists. When we know both the proportionate parts of the molecular weight which stand for aggregations of mass-units of the component elements, and the mass-unit weights of these elements given by the table, we can easily find the nearest whole numbers of mass-units which make up the molecular weights, and, putting them together, make the symbol.

Thus, we know by analysis that 100 parts by weight of water contain 11.18 parts by weight of hydrogen and 88.82 parts by weight of oxygen, while the approximate molecular weight of water, which is identical with the observed specific gravity of water vapor, referred to oxygen/32, is 18.02. The proportionate part of the molecular weight corresponding to each constituent, *i.e.* the total weight of the mass-units of each element present in the molecule, will evidently be given by the equations:

$$100 : 11.18 = 18.02 : x, \quad (x = 2.015)$$
$$100 : 88.82 = 18.02 : y, \quad (y = 16.005)$$

from which we find that one molecule of water consists of approximately 2.015 parts by weight of hydrogen united to 16.005 parts by weight of oxygen. Since 1 mass-unit of hydrogen weighs 1.0075 it is plain that a molecule of water must contain 2.015 ÷ 1.0075, obviously 2 mass-units of hydrogen; and, in like manner, since a mass-unit of oxygen weighs 16, it would seem that the water molecule must contain $\frac{16.005}{16}$ or 1 mass-unit of oxygen. The symbol of water is, therefore, H_2O.

In general, to find the molecular symbol of a compound:

(1) *Take the proportionate composition of the compound as given by analysis.*

(2) *Find the approximate molecular weight of the compound* (usually the specific gravity of the compound in gaseous condition referred to oxygen/32).

(3) *Calculate the approximate total weights of the mass-units of each constituent present in the molecule.*

(4) *Find approximately the number of mass-units of each kind present in the molecule, by dividing the total weight of the mass-units of each constituent by the mass-unit weight of that constituent, and accepting as the true numbers of mass-units present the whole numbers which stand nearest to the numbers found by the calculation.*

(5) *Make up the symbol of the molecule by putting together the symbols of the entire number of mass-units of all kinds.*

Calculations from Molecular Symbols of Compounds. The molecular symbol of a compound indicates, like the equivalent symbol, the *composition of the compound* and, more particularly, the *composition of a molecule* of the compound, viz.:

(1) The kinds of mass-units present in the molecule;

(2) The number of mass-units of each kind in the molecule;

(3) The total weight, in terms of oxygen taken as 16, of the mass-units of each kind in the molecule;

(4) The total weight, in terms of oxygen taken as 16, of all the mass-units in the molecule, *i.e.* the molecular weight;

(5) The proportionate composition, by weight, of the molecule in any system of units, *e.g.* the percentage composition;

(6) The ideal specific gravity referred to oxygen/32 of the gaseous compound, numerically equal to the molecular weight.

Since, moreover, any given quantity of a compound is an aggregation of molecules of the same kind and composition, it follows that the molecular symbol of a compound indicates, like the equivalent symbol, the *composition of any given quantity of that compound*, viz.:

(1) The constituent elements in the compound;

(2) The proportionate composition, by weight, of the compound in any system of units, *e.g.* the percentage composition;

(3) The gram-molecule, or the number of grams which will fill as much space as 32 grm. of oxygen, or 22.4 liters.

Thus, we have found for water the symbol H_2O, from which we know that the molecule of water contains mass-units of hydrogen and of oxygen; that it contains two hydrogen mass-units and one oxygen mass-unit; that the total weight of the hydrogen mass-units in the molecule is 2 × 1.0075 or 2.015, and that the total weight of oxygen in the molecule is 16; that the molecular weight is 2.015 + 16 or 18.015, in terms of oxygen taken as 16; and that the proportionate composition of a molecule of water, in any system of weights, is as 2.015 parts of hydrogen to 16 parts of oxygen; or, reducing the ratio to percentages, 11.18 per cent. of hydrogen to 88.82 per cent. of oxygen; and that if water were in the condition of an ideal gas, its specific gravity, referred to oxygen/32, should be 18.015. We know, further, from the molecular symbol, that any quantity of water, whenever and wherever found, is composed of hydrogen and oxygen, combined in the proportion of 2.015 parts by weight of hydrogen to 16 parts by weight of oxygen, or of 11.18 per cent. of hydrogen and 88.82 per cent. of oxygen, and that 18.015 grm. of gaseous water, viz., a gram-molecule, fills 24.4 liters.

Calculations from Equations of Molecular Symbols.

When the molecular symbols of gaseous substances are known, it is desirable to use them rather than equivalent symbols in expressing reactions in which such substances take part; for, *equations made up of molecular symbols of gaseous substances convey direct information as to the volumes of the given substances in addition to such other information as is conveyed by equations made up of equivalent symbols.*

Thus, the formation of water by the combination of hydrogen and oxygen is properly expressed by symbols showing these substances in molecular condition — namely, the symbols H_2, O_2, and H_2O. So the equation which represents the combination of 2.015 grm. of hydrogen and 16 grm. of oxygen to form 18.015 grm. of water is written

$$2\ H_2 + O_2 = 2\ H_2O$$

and this equation expresses the fact that 2 gram-molecules of hydrogen combine with 1 gram-molecule of oxygen to form 2 gram-molecules of water. Now, every gram-molecule of gaseous substances represents approximately a volume of 22.4 liters under standard conditions. So the equation expresses the fact that 2 × 22.4 liters of hydrogen combine with 22.4 liters of oxygen to form 2 × 22.4 liters of water under standard conditions; or, in general, that 2 volumes of hydrogen combine with 1 volume of oxygen to form 2 volumes of gaseous water. This, it will be remembered, was an observation of experiment.

We might also approach the establishment of the equation from the opposite direction. Knowing by experiment that 2 volumes of hydrogen combine with 1 volume of oxygen to form 2 volumes of gaseous water, and that, since in equal volumes of gaseous substances under the same conditions there are equal numbers of molecules, *the ratio of these volumes also expresses the ratio of the numbers of molecules involved*, we may put in an equation the numbers of molecules which represent the respective volumes:

$$2\ H_2 + O_2 = 2\ H_2O$$

Similarly, we may represent the combining of hydrogen and chlorine to form hydrogen chloride, so that the equation expresses at the same time the proportions by weight and the proportions by volume in which these gaseous substances combine:

$$H_2 + Cl_2 = 2\ HCl$$

In equations involving a gaseous substance with other non-gaseous substances, the relation of the volumes of the gaseous substances involved with equivalents of other non-gaseous substances appears.

Thus, in the equation

$$3\ Cu + 8\ HNO_3 = 3\ Cu(NO_3)_2 + 4\ H_2O + 2\ NO$$

the symbol 2 NO represents a gaseous substance. For every 3 gram-equivalents of copper 2 gram-molecules of NO will be set free. *But every gram-molecule of a gaseous substance represents a volume of 22.40 liters under standard conditions.* So for every gram-equivalent of copper a volume of $\frac{2}{3}$ × 22.4 liters or 14.97 liters of nitrogen dioxide will be liberated. It is obvious that the use of molecular symbols is of considerable advantage when relations of the volumes of gaseous substances are to be discussed.

It is of interest to note that the equation which represents by molecular symbols the combination of hydrogen and oxygen to form water, shows that *the oxygen molecule is divided into two mass-units in the process*, each of which enters into union with two mass-units of hydrogen; and similarly in the equation which shows the formation of hydrogen chloride from hydrogen and chlorine, we see the fact expressed that *every molecule of hydrogen and every molecule of chlorine is divided into two mass-units*, a mass-unit of each combining with a mass-unit of the other to form a molecule of hydrogen chloride.

Molecular Weight of Solids and Liquids.

For determining *the molecular condition, or the molecular weight, of substances existing as pure solids or pure liquids*, we are able in certain special cases to draw some conclusions, but as yet we have no simple and general method for accomplishing this very desirable end. We are able, however, to get an idea in many cases as to what the molecular condition of a solid or liquid individual substance is after it has been dissolved in a suitable liquid medium, which, however, must have no chemical action upon the dissolved substance. It appears in the case of certain individual substances, that when weights proportional to the equivalents, or the gram-molecular weights, of the substances are dissolved in certain solvents, certain physical properties of the solutions are manifested to the same degree.

Osmotic Pressure of Solutions.

The phenomenon known as *osmotic pressure of solution* is especially noteworthy in this connection. When an empty porous cup of unglazed porcelain is partially submerged in water, the water is free to pass through the porous medium; and even when the pores of such a cup are filled with a suitable deposit, like copper ferrocyanide, water is still able to pass while certain dissolved substances are unable to do so. Now if the cup with its pores filled with copper ferrocyanide is charged with the solution in water of such a dissolved substance, and closed by a tightly fitted stopper to which a pressure gauge is fitted, and the whole is then submerged in pure water, water passes from outside the cup into the inside and accumulates in the inside until the amounts of water passing inward and outward have become equal, while the gauge shows pressure within the cup. Since the water is pressing equally inward and outward, the pressure developed within the cup must be due, at least in the case of solutions in which no chemical action between the solvent and the solute takes place, to some specific action of the solute. *This pressure of the solution upon the semi-permeable wall is called the osmotic pressure.*

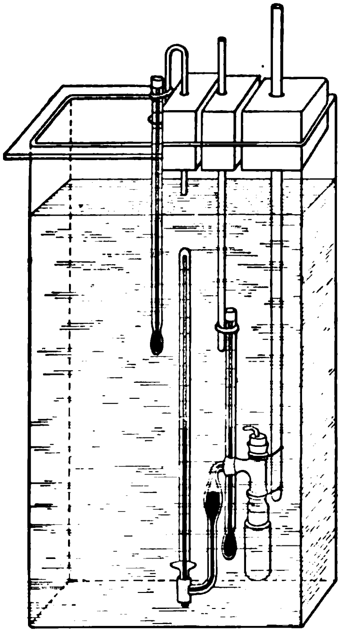


FIG. 42. — Apparatus for measuring Osmotic Pressure.

The study of osmotic pressures has led to the generalization, first advanced by Van't Hoff, that the osmotic pressures observed in solutions are closely related to the concentration of the molecules of the solutes, and to the conclusion that *whatever the real nature of the process of solution may be, the molecules of a solute diffused through a solvent appear to be obedient to certain rules which have great similarity to the laws of Boyle and Charles, and the hypothesis of Avogadro.*

Thus, with regard to the class of *non-electrolytic substances* — that is, those substances which do not conduct the electric current in water solution, it appears that

(1) *The osmotic pressure of the solution of an individual non-electrolyte is proportional to the concentration, and inversely proportional to the volume, occupied by a given mass;*

(2) *The osmotic pressure varies with the temperature and seemingly in direct proportion to the absolute temperature;*

(3) *Solutions of non-electrolytes which at the same temperature exert the same osmotic pressure appear to contain the same numbers of individual active units or molecules in a given volume.*

For example, at a fixed temperature, the osmotic pressure of a solution of cane sugar, a non-electrolyte, is proportional to the concentration; and for a fixed concentration it increases with the temperature; and under fixed conditions of temperature and concentration it shows a definite value, which we may proceed to compare with the gas pressure of a gas occupying the same volume as the volume of the solution and at the same temperature as the solution.

Thus, Pfeffer found that at 6.8° a water solution of cane sugar, $C_{12}H_{22}O_{11}$, containing 10 grm. in 1 liter, gave an osmotic pressure of 505 mm. of mercury. A gram-equivalent of cane sugar, 342.16 grm., dissolved in 34.216 liters, would therefore give at the same temperature the same pressure. Now, the volume occupied by 1 gram-molecule of oxygen, and other gaseous substances, is 22.4 liters at 0° and 760 mm., and the volume occupied by these gases at 6.8° and 505 mm. may be calculated by the formula,

$$V = \frac{p_0 v_0 T}{p\ 273} = \frac{760 \times 22.4 \times 279.8}{505 \times 273} = 34.55$$

So we find that the volume occupied by a gram-equivalent of cane sugar in water solution proves to be 34.55 liters, practically the same as that occupied by a gram-molecule of oxygen under the same conditions of temperature and pressure.

We have in this fact, making the reasonable assumption that the simple equivalent of sugar, represented by the simplest possible symbol, $C_{12}H_{22}O_{11}$, is identical with the molecule of sugar, a basis for the inference that *in equal volumes of the water solution of cane sugar and of gaseous oxygen there are, under the same conditions of temperature and pressure, the same number of molecules.*

Abnormal Osmotic Pressure of Solutions of Non-electrolytes.

Van't Hoff showed that to solutions of non-electrolytic substances, like the cane sugar, the general expression for the gas laws,

$$pv = RT$$

may be directly applied; but that *in the case of electrolytic substances, like acids, bases, and salts, the osmotic pressures are always greater than would be expected,* so that the general expression for the laws of solution takes the form,

$$pv = iRT,$$

in which i is the coefficient, always greater than unity, and depending upon the substance under examination, and also upon the dilution, until a certain dilution is reached, at which i attains its maximum value.

Dissociation in Solution. This deviation from the rule, on the part of many substances in solution, is easily explained if we assume the formation in solution of a larger number of active units, or molecules, — a kind of *dissociation in solution*, which produces the effect of increased osmotic pressure, just as dissociation by heat produces increased gas pressure proportionate to the number of new molecules. To Arrhenius we owe the suggested explanation of this phenomenon of solution in the breaking down of compounds into free electrically charged ions, while Reychler postulates the formation of new units by a kind of hydrolytic action involving also an interchange of electrical charge between the molecules. These are points to which we shall recur. For the present it is sufficient to see that the peculiar behavior of electrolytes in solution as regards osmotic pressure is explicable upon the hypothesis of some sort of molecular splitting with formation of a greater number of active units.

Osmotic Pressure and Gas Pressure. The determination of the molecular condition of solutes by direct observation of the osmotic pressures is very difficult, and in many cases impracticable. We have, however, certain methods founded upon experiment, but now shown by Van't Hoff to be justified upon the assumption that *osmotic pressure is of the same nature as gas pressure*, for the comparison of the numbers and weights of the active units in solutions.

Depression of Freezing Points of Solutes. *Thus we know that when a substance is dissolved in a liquid, the freezing point of the liquid is invariably lowered.* The depression of the freezing point of the solvent proves to be proportional to the amount of material dissolved, and it was found by Raoult that *for a large number of non-electrolytic substances of known molecular weight in the gaseous condition, and for several solvents, the depression of the freezing point of a given amount of solvent is the same for a gram-molecule of each substance, but the exact amount of such gram-molecular depression of the freezing point depends upon the nature of the solvent.*

Molecular Lowering of Freezing Point. If Δ is the observed depression of the freezing point when w grm. of a solute are dissolved in 1000 grm. of the solvent, m being the molecular weight of the solute, and C the *molecular lowering*, or the depression of the freezing point of the solvent produced by a gram-molecule of the solute in 1000 grm. of solvent, we have

$$C : m = \Delta : w$$

Whence the molecular lowering for the given solvent is given by the expression,

$$C = \frac{m\Delta}{w}$$

Raoult found the *molecular lowering for water to be in the average 1.85° for every gram-molecule of non-electrolyte dissolved in 1 liter of water.*

Upon the supposition that osmotic pressure and gas pressure are of the same nature, it has been shown by Van't Hoff that the depression of the freezing point of water by 1 gram-molecule of solute in 1 liter of solvent should be 1.88° for water, 3.88° for acetic acid, and 4.90° for benzene, values which are closely in accord with Raoult's experimental results.

Molecular Weights of Non-electrolytes in Solution.

Knowing the molecular lowering, it is possible to find the molecular weight of any non-electrolyte by determining the weight of that substance which produces the molecular lowering in a given solvent. If Δ is the observed depression of the freezing point, m the molecular weight to be determined, C the molecular lowering of the solvent, W the weight of the solvent, and w the weight of the solute, then, when the weight of solvent is 1000 grm.,

$$C : m = \Delta : w,$$

and

$$m = \frac{wC}{\Delta}$$

For any other weight of solvent, W,

$$m = \frac{1000\, wC}{\Delta W}$$

By means of this formula, *the molecular weight of a non-electrolyte in a given solvent may be found from the molecular lowering and the depression of the freezing point observed for the solution of a known weight of solute in a known weight of solvent.*

For example, it was found experimentally that 1 grm. of carbon tetrachloride dissolved in 100 grm. of acetic acid lowered the freezing of the solvent 0.252°. From the formula we have

$$m = \frac{1000 \times 1 \times 3.88}{0.252 \times 100} = 154$$

which accords with the molecular weight 153.8 deduced from the equivalent symbol CCl_4, and the specific gravity to oxygen / 32.

It should not be forgotten, however, that the molecular weight found for a non-electrolyte in a certain solvent is not necessarily the molecular weight which it may have in another solvent, or in gaseous condition. Methyl alcohol, for example, showed in water a molecular weight of about 32, corresponding to the symbol CH_4O, while in benzene its molecular weight proved to be 50 per cent. greater, which means, apparently, that molecules of CH_4O and $C_2H_8O_2$ exist in about equal proportions in benzene under the conditions of the experiment.

Elevation of Boiling Points of Solutes.

It has been found also that *when a substance is dissolved in a liquid, the boiling point of the liquid is invariably raised.* The elevation of the boiling point of the solvent is proportional to the amount of material dissolved, and it appears to be the case that *the rise of the boiling point of a given amount of solvent is the same for a gram-molecule of every non-electrolyte, the exact amount of such rise depending upon the nature of the solvent.*

Molecular Rise of Boiling Point.

If we let C stand for the *molecular rise* or the rise of the boiling point of the solvent produced by a gram-molecule of a non-electrolyte in 1000 grm. of a given solvent, m for the molecular weight of a non-electrolyte, w for the weight of solute used in any given experiment in a weight W of solvent, and R for the observed rise of the boiling point, we may develop a formula similar to the formula which gives the molecular weight from the depression of the freezing point,

$$m = \frac{1000\, wC}{RW}.$$

Molecular Weight of Non-electrolytes in Solution.

Whence, *knowing the molecular rise, it is possible to find the molecular weight of a non-electrolyte in any given solvent from the rise of the boiling point observed for the solution of a known weight of solute in a known weight of solvent.*

Thus, 1 grm. of naphthalene, dissolved in 100 grm. of ether, raised the boiling point of the latter 0.163°. The molecular rise for ether is 2.11°. Then,

$$m = \frac{1000 \times 1 \times 2.11}{0.163 \times 100} = 129.4$$

a value which is closely approximate to 128.06, the molecular weight of naphthalene in gaseous condition, and corresponds to the symbol $C_{10}H_8$.

It is of interest to note that Van't Hoff has been able to deduce, from theoretical considerations, for the *molecular depression of the freezing point* of a solvent, or the depression produced by 1 gram-molecule of a non-electrolyte in 1000 grm. of solvent, and for the *molecular rise of the boiling point* of a solvent, or the rise produced by 1 gram-molecule of non-electrolyte in 1000 grm. of solvent, the same form of expression,

$$C = \frac{2\,T^2}{1000\,L}$$

in which C is the molecular depression or rise, T the absolute temperature of the freezing point or boiling point of the solvent, and L the latent heat of fusion or of vaporization, respectively, for 1 grm. of the solvent.

It is, of course, plain that the molecular symbol of a substance in solution may be computed from the discovered molecular weight, the percentage composition, and the mass-unit weights of the elements, by a method precisely similar to that employed in determining the molecular symbol of a gaseous substance from the specific gravity to oxygen /32, the percentage composition, and mass-unit weights of the elements.

Abnormal Depression of Freezing Point and Rise of Boiling Point of Solutions of Electrolytes.

In the case of *electrolytes* in solution, experience shows, as we have seen, that an abnormally large osmotic pressure develops. *We note, also, in the depression of the freezing points and in the rise of the boiling points of solutions containing electrolytes, abnormally large depressions and rises, respectively, which are naturally attributed to a multiplication of active units.* Given the depression of the freezing point or rise of the boiling point of a solvent of known molecular lowering or rise for non-electrolytes, it is possible to deduce the amount of such multiplication of active units which takes place in the solution of electrolytes. Thus, the molecular lowering observed when 1 gram-molecule of a non-electrolyte dissolves in 1000 grm. of water is shown in the expression

$$C = 1.88^\circ$$

When the molecule of an electrolyte divides, the observed depression of the freezing point will depend upon the amount of the division. The formation of two active units from one molecule will double the depression, and the formation of i units from a molecule will produce i times the molecular depression. So, when t is the observed depression of the freezing point for a gram-molecule of an electrolyte, and i the number of the active units resulting from a molecule in the process of solution,

$$i \times 1.88 = t$$

and

$$i = \frac{t}{1.88}$$

This i is Van't Hoff's coefficient i in the general expression,

$$pv = iRT$$

and expresses the *ratio between the osmotic pressure actually observed and the pressure which would be exerted were there no division of the molecule in the process of solution.* This i is the ratio of the sum of the numbers of unbroken molecules and active units of division to the number of original molecules.

The table shows some of the values found for i in the case of the solution of several electrolytes in water, t being the observed depression of the freezing point caused by 1 gram-molecule of the solute in 1000 grm. of water:

OSMOTIC PRESSURE OF ELECTROLYTES

ELECTROLYTE	SYMBOL	$i = \frac{t}{1.88}$
Sodium chloride	$NaCl$	1.87
Potassium chloride. . . .	KCl	1.79
Potassium nitrate	KNO_3	1.64
Barium chloride	$BaCl_2$	2.58
Sodium hydroxide	$NaOH$	1.93
Potassium hydroxide . . .	KOH	1.88
Barium hydroxide	$Ba(OH)_2$	2.64
Hydrochloric acid	HCl	1.95
Nitric acid	HNO_3	1.91
Sulphuric acid	H_2SO_4	2.02

These values for i indicate some action of water, the solvent, by which more active units are produced from the single molecules of the substances named. This is obviously a process somewhat analogous to the dissociation of ammonium chloride in the gaseous state by heat.

Experimental Determination of Depression of Freezing Point and Elevation of Boiling Point.

For *the experimental determination of the depression of the freezing point and rise of the boiling point of solutions by addition of solutes* many ingenious forms of apparatus have been devised. *Beckmann's device* for determining the depression of the freezing point is shown in the figure. The tube A, containing the solvent, a thermometer T, a stirrer S, and the solute introduced at will through the side tube, is fitted to A_1 so that an air space is left between the tubes. This system is immersed in a suitable freezing mixture contained in B which is also provided with a stirrer.

Knowing the weight of solvent W contained in the tube and the weight w of the solute introduced, the molecular lowering of the solvent C, the observed depression, Δ, of the freezing point of the solvent in consequence of the addition of the solute, we have the necessary data for calculating the molecular weight of the solute in the given solution.

A simple and improved form of apparatus for determining the rise of the boiling point is that devised by *Jones*. The tube A is connected with the condenser C and contains a known weight W of the solvent, a known weight w of solute, the thermometer, and a platinum shield to protect the thermometer from the effect of the cooled liquid retained from the condenser. The tube is surrounded by asbestos, rests on wire gauze, and is heated by a small flame. The difference between the boiling point of the pure solvent and that observed for the solution is the observed rise R. When C the molecular rise of the solvent is known, the data are at hand for the calculation of the molecular weight of the solute according to the formula given.

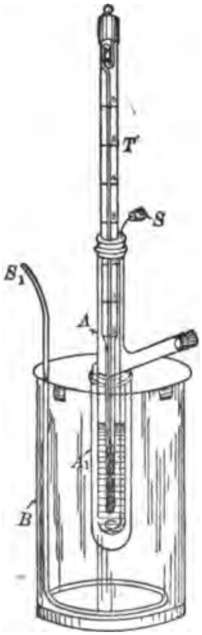


FIG. 43.—Beckmann's Apparatus for measuring Depression of Freezing Point.

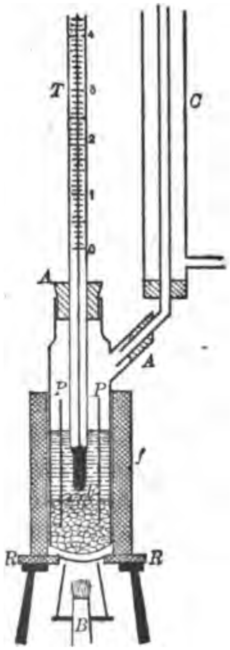


FIG. 44.—Jones' Apparatus for measuring Rise of Boiling Point.

CHAPTER XIV

VALENCE

Combining Power of Mass-units for Hydrogen.

HAVING determined the molecular weights of substances, the mass-unit weights of the elements, and molecular symbols for both elements and compounds, some further relations of the mass-units of the elements come to light. Let us compare the molecular symbols of certain representative hydrogen compounds, containing hydrogen and one other element. In the molecule of gaseous hydrogen chloride, HCl, one mass-unit of hydrogen is combined with one mass-unit of chlorine, and the molecules of hydrogen bromide, HBr, and hydrogen iodide, HI, are similar to the molecule of hydrogen chloride in that they contain one mass-unit of the characteristic element combined with one mass-unit of hydrogen. *The mass-units of chlorine, bromine, and iodine possess individually the power of combining with one mass-unit of hydrogen.* Similarly, the molecules of gaseous hydrogen oxide, or water, H_2O, and of hydrogen sulphide, H_2S, each consist of one mass-unit of the characteristic element combined with two mass-units of hydrogen. *The mass-units of oxygen and sulphur obviously possess individually the power of combining with two hydrogen mass-units.* The molecular symbols of nitrogen hydride or ammonia, H_3N, phosphorus hydride, H_3P, and arsenic hydride, H_3As, show that *single mass-units of nitrogen, phosphorus, and arsenic each have the power of combining with three hydrogen mass-units.* The molecular symbols of carbon hydride or methane, H_4C, and silicon hydride, H_4Si indicate that *carbon and silicon mass-units each possess the power of combining with four hydrogen mass-units.*

It appears, therefore, that *the mass-units of certain elements possess different powers for holding in combination hydrogen mass-units in molecules of hydrogen compounds.* The combining powers of the mass-units of certain elements for hydrogen mass-units are shown in the table:

COMBINING POWERS OF MASS-UNITS OF ELEMENTS FOR HYDROGEN MASS-UNITS

ELEMENT	HYDROGEN COMPOUND	COMBINING POWER
Chlorine	HCl	I
Bromine	HBr	
Iodine	HI	
Oxygen	H_2O	II
Sulphur	H_2S	
Nitrogen	H_3N	III
Phosphorus	H_3P	
Arsenic	H_3As	
Carbon	H_4C	IV
Silicon	H_4Si	

Many of the elements which combine with hydrogen are capable of combining with one another to form compounds for which we may write molecular symbols. Thus we have iodine chloride, ICl, similar to hydrogen chloride, HCl; sulphur chloride, Cl_2S, similar to hydrogen sulphide, H_2S; phosphorus chloride, Cl_3P, similar to phosphorus hydride, H_3P, and carbon chloride, Cl_4C, similar to carbon hydride, H_4C. *The mass-units of certain elements which have the power of combining with a definite number of mass-units of hydrogen may show the same power for combining with mass-units of elements other than hydrogen.*

Valence. *The power of the mass-unit of one element to hold in combination a definite number of mass-units of another element we call the valence of the element; and, assuming the valence of hydrogen to be I, we express the valence of other elements in terms of the valence of hydrogen.*

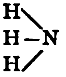
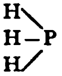
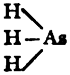
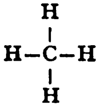
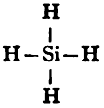
Thus we say that in hydrogen chloride, HCl, chlorine has a valence of I, since one mass-unit of chlorine is in combination with one mass-unit of hydrogen, and for similar reasons we say that in hydrogen bromide, HBr, and hydrogen iodide, HI, bromine and iodine each have a valence of I. So also we may say that in hydrogen oxide, H_2O, oxygen has a valence of II, that in nitrogen hydride, NH_3, nitrogen has a valence of III, and that in carbon hydride, CH_4, carbon has a valence of IV, while in corresponding hydrogen compounds sulphur has a valence of II, phosphorus and arsenic have a valence of III, and silicon a valence of IV. In like manner, in iodine chloride, ICl, both iodine and chlorine have the valence I, in sulphur chloride, Cl_2S, chlorine has the valence I and sulphur the valence II, in phosphorus chloride, Cl_3P, chlorine has the valence I and phosphorus the valence III, while in carbon chloride, Cl_4C, chlorine has the valence I and carbon the valence IV.

In expressing the valence of an element it is convenient to make use of the Latin derivatives, and to say that in the hydrogen compounds, and the other compounds which we have mentioned, hydrogen, chlorine, bromine, and iodine are *univalent*, oxygen and sulphur are *bivalent*, nitrogen, phosphorus, and arsenic are *trivalent*, and that carbon and silicon are *quadrivalent*.

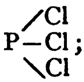
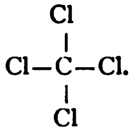
Variation in Valence. If we extend our investigation, we find that *in many cases the valence of the elements appears to vary with conditions and association.* Whenever we see a varying power of combination between hydrogen and other elements, or between oxygen and other elements, we assume that it is the valence of the other elements which is variable. *Hydrogen always has a valence of I and oxygen ordinarily has a valence of II*, while the valence of elements other than hydrogen and oxygen does not always appear to be the same in different compounds. We know of but one hydrogen compound of chlorine, hydrogen chloride, HCl, and in this compound chlorine is univalent; in chlorine monoxide, Cl_2O, also, the chlorine is univalent; but besides chlorine monoxide we know other compounds of chlorine in which its valence appears to be III, V, and even VII. Sulphur is bivalent in hydrogen sulphide, H_2S, quadrivalent in sulphur dioxide, SO_2, and sextivalent in sulphur trioxide, SO_3. Nitrogen appears to be trivalent in ammonia, NH_3, and pentavalent in ammonium chloride, NH_4Cl, while carbon is quadrivalent in carbon dioxide, CO_2, and bivalent in carbon monoxide, CO.

Graphic Symbols. Heretofore in our molecular symbols, such as H_2, O_2, H_2O, we have made no attempt to indicate by any sign the valence of the constituent mass-units of the molecules. In the mass-unit symbols, such as H, O, N, C, it is sometimes convenient to indicate valence by affixing to the mass-unit symbol a Roman numeral corresponding to the valence. Thus H^{I} means that hydrogen is univalent, O^{II} that oxygen is bivalent, N^{III} that nitrogen is trivalent, C^{IV} that carbon is quadrivalent. Or, it may best serve our purpose to represent valence by affixing to the mass-unit symbols ***bonds***, or lines, each bond or line representing one unit of valence, or, we may say, one ***affinity***. ***Symbols in which the valence is indicated by bonds are called graphic symbols.*** Thus we may represent the mass-unit of hydrogen by the symbol H—, that of oxygen by the symbol O=, or —O— ; that of nitrogen by the symbol N≡, or =N—, or $-\overset{|}{N}-$; and that of carbon by the symbol C$\equiv$, or =C=, or $-\overset{|}{\underset{|}{C}}-$. The molecule of hydrogen we may represent by the symbol H—H, the molecule of oxygen by the symbol O=O, and the molecule of water by the symbol $\begin{matrix}H\\H\end{matrix}\!\!>\!O$, or H—O—H. In these graphic symbols the manner of arrangement of the bonds about the mass-unit symbols is a matter of convenience only.

Graphic Molecular Symbols of Hydrogen Compounds

Compound	Common Symbol	Graphic Symbol
Hydrogen chloride	HCl	H—Cl
Hydrogen bromide	HBr	H—Br
Hydrogen iodide	HI	H—I
Hydrogen oxide	H_2O	H—O—H
Hydrogen sulphide	H_2S	H—S—H
Ammonia	H_3N	
Phosphorus hydride	H_3P	
Arsenic hydride	H_3As	
Methane	H_4C	 $H-\overset{H}{\underset{H}{C}}-H$
Silicon hydride	H_4Si	 $H-\overset{H}{\underset{H}{Si}}-H$

By means of graphic symbols thus constructed the relations of the mass-units in the molecules of the hydrogen compounds of the preceding table are clearly brought to light.

Similarly we may write graphic symbols for the compounds of chlorine, iodine, sulphur, carbon, and silicon with one another. Thus we have iodine chloride, I—Cl; sulphur chloride, Cl—S—Cl; phosphorus chloride,  $P\begin{array}{l}/Cl\\ -Cl\\ \backslash Cl\end{array}$; and carbon chloride,  $\begin{array}{c}Cl\\ |\\ Cl-C-Cl\\ |\\ Cl\end{array}$.

Satisfaction of Affinities in Molecules of Elements.

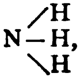
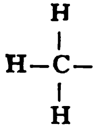
In most elementary molecules consisting of two mass-units of odd or even valence, affinities of different mass-units of the same kind satisfy one another.

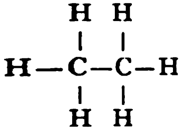
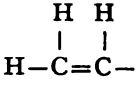
Thus, in the molecule of hydrogen, H—H, we conceive the two mass-units, H— and —H, to be united to each other by a single affinity; two mass-units of oxygen, O= and =O, are united in one oxygen molecule, O=O, each mass-unit being linked to the other by two affinities; and two mass-units of nitrogen may be represented as united to one another by three affinities in the molecule of nitrogen, N≡N.

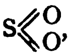
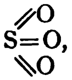
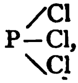
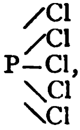
In a few elementary molecules, which consist of one mass-unit of even valence, we have instances of affinities of the same mass-units satisfying one another. Thus we may consider that in the zinc molecule the two affinities satisfy one another, as shown in the symbol $Zn\supset$, or $\boxed{Zn}$, and similarly we may represent the molecule of Cadmium by the symbol $Cd\supset$, and the mercury molecule by the symbol $Hg\supset$.

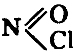
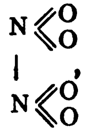
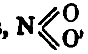
Satisfaction of Affinities in Molecules of Compounds.

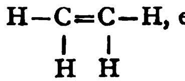
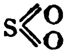
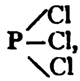
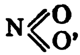
In the molecules of compounds the affinities of mass-units may be satisfied by the affinities of other mass-units, of different kinds or of the same kind.

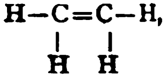
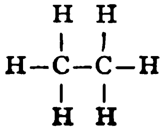
Thus, in the molecule of hydrogen chloride, H—Cl, two different mass-units are linked together by the union of single affinities. In one molecule of water, H—O—H, two hydrogen mass-units, H— and —H, and one oxygen mass-unit, —O—, are represented as combined, the molecular symbol indicating that the two affinities of the oxygen mass-unit are satisfied by the affinities of two hydrogen mass-units; in one molecule of ammonia,  $N\begin{array}{l}/H\\ -H\\ \backslash H\end{array}$, the affinities of three hydrogen mass-units satisfy the three affinities of one nitrogen mass-unit; while in the molecule of methane,  $H-\overset{H}{\underset{H}{C}}-H$, the four affinities of one carbon mass-unit are satisfied by the four affinities of four hydrogen mass-units.

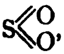
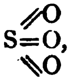
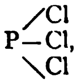
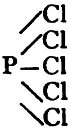
In many compounds of carbon, each of two mass-units of carbon is held to the other with mutual satisfaction of affinities: in ethane,  $H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$, by one affinity; in ethylene,  $H-\overset{H}{C}=\overset{H}{C}-H$, by two affinities; and in acetylene, $H-C\equiv C-H$, by three affinities.

Odd and Even Valence. It has been pointed out that in many cases we must consider an element to have different valences in different compounds. *In the case of elements of more than one valence it appears that the different valences may usually be represented by odd or even numbers which differ from one another by two.* Thus, in sulphur dioxide, , sulphur is quadrivalent, and in sulphur trioxide, , it is sextivalent. In phosphorus trichloride, , phosphorus is trivalent, while in phosphorus pentachloride, , phosphorus is quinquivalent. The valences of sulphur are represented by even numbers, differing from one another by two, and the valences of phosphorus are represented by odd numbers differing from one another by two.

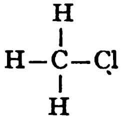
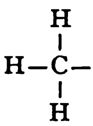
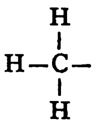
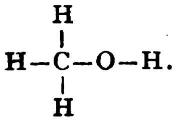
Under certain conditions, however, certain elements may exhibit both odd and even valences in different combinations. Thus in nitrosyl chloride, , nitrogen is represented with a valence of III, while in nitrogen dioxide, N=O, which may be formed from nitrosyl chloride by heating, the valence of nitrogen appears as II. So also in nitrogen tetroxide at low temperatures,  O_2N-NO_2, nitrogen has a valence of V, while in the dissociated nitrogen tetroxide of moderate temperatures, , we give nitrogen a valence of IV. In the case of nitrogen the valences III and V are the *prevailing valences* of nitrogen in most of its compounds, whereas the valences II and IV in the examples shown are exceptional for nitrogen.

Latent Affinities. *Molecules of many compounds in which mass-units of the same kind are linked together by mutual satisfaction of affinities, and molecules of many compounds in which the characteristic elements exhibit less than their maximum valences, are said to possess latent affinities.* Thus, in ethylene,  $H-\underset{H}{\underset{|}{C}}=\underset{H}{\underset{|}{C}}-H$, each carbon mass-unit has one latent affinity, while in acetylene, $H-C\equiv C-H$, two affinities of each carbon mass-unit are latent. In sulphur dioxide, , sulphur has two latent affinities; in phosphorus trichloride, , phosphorus has two latent affinities; in nitrogen dioxide, $N=O$, nitrogen has three latent affinities, and in dissociated nitrogen tetroxide, , nitrogen has one latent affinity.

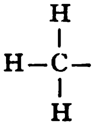
Saturated and Unsaturated Molecules. *A molecule in which there are no latent affinities is said to be saturated; while a molecule which has one or more latent affinities is unsaturated.* Thus, the molecule of acetylene, $H-C\equiv C-H$, is unsaturated, because by the direct addition of mass-units of hydrogen, ethylene,  $H-\underset{H}{\underset{|}{C}}=\underset{H}{\underset{|}{C}}-H$, unsaturated in less degree, and the completely saturated ethane,  $H-\overset{H}{\overset{|}{\underset{H}{\underset{|}{C}}}}-\overset{H}{\overset{|}{\underset{H}{\underset{|}{C}}}}-H$, may result. In the molecule of ethane the two carbon mass-units are held together each by a single affinity, and further addition of hydrogen, if such addition could be made, would break down the molecule into two molecules of methane.

The molecule of sulphur dioxide, , is unsaturated because by direct addition of oxygen it may pass into the saturated molecule of sulphur trioxide, , and the molecule of phosphorus trichloride, , is unsaturated because by direct addition of chlorine it may pass into the saturated molecule phosphorus pentachloride, .

In the saturation of the acetylene molecule by addition of hydrogen the latent affinities of carbon become active; and similarly the saturation of the sulphur dioxide molecule by addition of oxygen and the saturation of the phosphorus trichloride molecule by addition of chlorine bring into activity the latent affinities of sulphur and phosphorus. We frequently speak of compounds like acetylene, sulphur dioxide, and phosphorus trichloride, whose molecules are unsaturated, as *unsaturated compounds*, while compounds whose molecules are saturated are called *saturated compounds*.

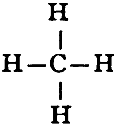
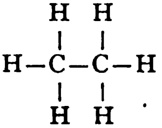
Radicals. Sometimes we may conveniently consider portions of molecules as units for purposes of discussion, without considering whether they actually exist out of combination. For example, we may set apart the group $-O-H$ and speak of its union with the mass-unit $H-$ to form $H-O-H$, or in the compound  $H-\overset{H}{\underset{H}{C}}-Cl$ we may speak of the union of the group  $H-\overset{H}{\underset{H}{C}}-$ with $-Cl$. Or we may speak of the union of the group $H-O-$ with the group  $H-\overset{H}{\underset{H}{C}}-$ to form  $H-\overset{H}{\underset{H}{C}}-O-H$. *Such parts of molecules, set apart for conven-*

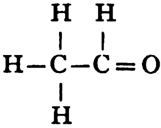
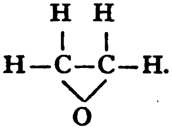
ience, and regarded as possessing free affinities and capable of uniting with mass-units or with other parts of molecules, we call radicals.

Thus $-O-H$ and  $\begin{array}{ccc} & H & \\ & | & \\ H- & C & - \\ & | & \\ & H & \end{array}$ are univalent radicals known as *hydroxyl* and *methyl* respectively.

Ions. The *electrically charged parts of molecules, or ions,* which appear in processes of electrolysis, and which take part in reactions, have certain latent powers of combination, and may therefore be represented in the same manner that we represent radicals. Thus the symbols $\overset{+}{Na}$ and $\overset{-}{Cl}$ represent ions of the assumed molecule $Na-Cl$, and $2\overset{+}{K}$ and $\overset{-}{=}[PtCl_6]$ stand for ions of the assumed molecule K_2PtCl_6.

The Hydroxyl-ion. Since the hydrogen-oxygen-ion, $-O\overset{-}{-}H$, which we have followed in many reactions, is identical in its mass-units with the radical hydroxyl, it is conveniently designated as the *hydroxyl-ion.*

Relationship of Mass-units in Molecules. *The use of graphic symbols leads to the notion of constitution, or definite relationship of mass-units, of molecules.* In the molecule, $H-O-H$, it is plain that the oxygen mass-unit links together the hydrogen mass-units, and so serves a purpose different from that shown by either hydrogen mass-unit; so also in the molecule  $\begin{array}{ccc} & H & \\ & | & \\ H- & C & -H \\ & | & \\ & H & \end{array}$ the carbon mass-unit serves the purpose of binding the hydrogen mass-units to itself. In the molecule  $\begin{array}{cccc} & H & H & \\ & | & | & \\ H- & C- & C & -H \\ & | & | & \\ & H & H & \end{array}$ the relation of each carbon mass-unit to the molecule is the same as that of the other — each is linked to three hydrogen mass-units, and there is nothing to show that any hydrogen mass-unit has any different function from any other hydrogen mass-unit. Let us suppose, however, that two hydrogen mass-units are to be removed from the molecule, and substituted by one bivalent oxygen mass-unit.

The oxygen mass-unit may substitute two hydrogen mass-units joined to the same carbon mass-unit, giving  $\mathrm{H-\underset{H}{\overset{H}{C}}-\overset{H}{C}=O}$, or it may replace two hydrogen mass-units joined to different carbon mass-units, giving  These two symbols, which, when written empirically in the form C_2H_4O, appear to be identical, are in reality the symbols of two distinctly different compounds which may be formed by the substitution of one oxygen mass-unit for two hydrogen mass-units in the molecule of ethane, C_2H_6. Furthermore, we are led by the study of the behavior of these two substances in reactions to believe that in one of them the oxygen mass-unit stands in close relation to only one carbon mass-unit, while in the other the oxygen mass-unit is related closely to both carbon mass-units. *Such compounds as these, whose molecules are made up of the same numbers and the same kinds of mass-units, which, however, seem to be differently related within the molecules of the different compounds, are called isomeric compounds, or isomers, and the relation of isomers is called isomerism.*

Isomerism.

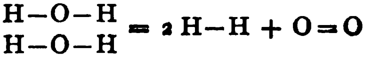
Graphic Equivalent Symbols.

While the development of the system of graphic notation implies in the first instance a knowledge of molecular symbols, after having learned something of the prevailing valences of certain elements in characteristic compounds *we may extend the use of the graphic notation to cover the equivalent symbols of certain substances containing elements of established valence.* It must be remembered, however, that *such graphic equivalent symbols, having been established by analogies only, give no information of actual molecular weights, and illustrate proportionate composition only.*

The Symbol for Water.

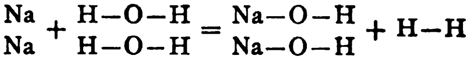
The symbol H—O—H is a molecular symbol representing the constitution and molecular weight of water in the gaseous condition. We have no right to assume that the molecule of water in the liquid condition or in the solid condition is represented by the symbol H_2O. On the contrary, we have evidence in certain physical relations which goes to show that the molecule weight of liquid water at

0° may correspond to the symbol $(H_2O)_4$. It is convenient, however, to use in dealing with the reactions of liquid water the symbol H_2O, which, in this case and so far as concerns the molecule of liquid water, is the equivalent symbol rather than the molecular symbol. The electrolysis of liquid water may, therefore, be shown in the expression,



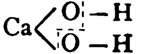
$$\begin{matrix}H-O-H\\H-O-H\end{matrix} = 2\,H-H + O=O$$

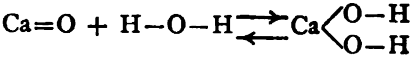
but we must recognize the fact that we are here dealing with the equivalent symbol of liquid water, though the symbols $H-H$ and $O=O$, for hydrogen and oxygen, represent the molecules of these elements evolved in gaseous condition. Similarly, the reaction between liquid water and sodium may be represented by the expression,



$$\begin{matrix}Na\\Na\end{matrix} + \begin{matrix}H-O-H\\H-O-H\end{matrix} = \begin{matrix}Na-O-H\\Na-O-H\end{matrix} + H-H$$

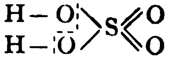
although the symbols for water in the liquid condition and for sodium hydroxide are equivalent symbols, the form of the latter being fixed by its obvious relation to the symbol of water. *In expressing relations by means of graphic symbols it is to be assumed that such symbols are equivalent symbols and represent only ideal molecules, unless we have specific knowledge that they represent determined molecular weights and therefore true molecules.*

Hydroxides and Oxides. Looking back over our former work, it is obvious that many of the relations which we have observed in the constitution of compounds may be advantageously expressed by the aid of graphic symbols. For example, *the relation between hydroxides and the oxides to which they correspond may be clearly brought out graphically.* Thus calcium hydroxide, $Ca(OH)_2$, containing the elements of calcium oxide, CaO, and of water, H_2O, is represented by the symbol  $Ca\begin{matrix}\diagup O-H\\ \diagdown O-H\end{matrix}$ and the fact that calcium hydroxide is formed by the union of the two oxides and again decomposable into them by heat, is shown in the equation,



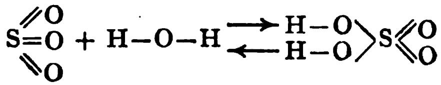
$$Ca=O + H-O-H \rightleftarrows Ca\begin{matrix}\diagup O-H\\ \diagdown O-H\end{matrix}$$

Similarly, sulphuric acid, H_2SO_4, derived from sulphur trioxide, SO_3, and water, H_2O, has its constitution shown by the symbol,



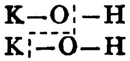
$$\begin{matrix}H-O\\H-O\end{matrix}\rangle S \langle\begin{matrix}O\\O\end{matrix}$$

and the reaction of formation and decomposition of sulphuric acid is shown by the equation,



$$S\left\langle\begin{matrix}=O\\=O\\=O\end{matrix}\right. + H-O-H \rightleftarrows \left.\begin{matrix}H-O\\H-O\end{matrix}\right\rangle S\left\langle\begin{matrix}=O\\=O\end{matrix}\right.$$

Similar relations become apparent for potassium hydroxide, KOH, when we write the symbols for two molecules of that compound,

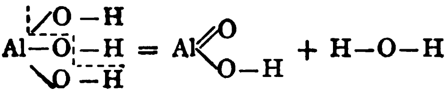


$$\begin{matrix}K-O-H\\K-O-H\end{matrix}$$

from which we see that it contains the elements of potassium oxide, K_2O, and water, H_2O, although potassium hydroxide does not decompose into these two oxides when heated.

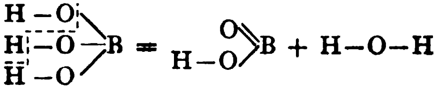
Normal Hydroxides and Oxy-hydroxides. *In some hydroxides the mass-units of the characteristic elements are combined with the maximum number of hydroxyl groups called for by the valence, and such hydroxides are called normal hydroxides, while other hydroxides which contain less than the maximum number of hydroxyl groups are known as oxy-hydroxides.* Thus, potassium hydroxide, K—O—H, calcium hydroxide, $Ca\left\langle\begin{matrix}O-H\\O-H\end{matrix}\right.$, and ferric hydroxide, $Fe\left\langle\begin{matrix}O-H\\O-H\\O-H\end{matrix}\right.$, are normal basic hydroxides; boric acid, $\left.\begin{matrix}H-O\\H-O\\H-O\end{matrix}\right\rangle B$, and orthosilicic acid, $\left.\begin{matrix}H-O\\H-O\\H-O\\H-O\end{matrix}\right\rangle Si$, furnish examples of normal acidic hydroxides; while the common acids, sulphuric acid, $\left.\begin{matrix}H-O\\H-O\end{matrix}\right\rangle S\left\langle\begin{matrix}=O\\=O\end{matrix}\right.$, and nitric acid, $H-O-N\left\langle\begin{matrix}=O\\=O\end{matrix}\right.$, furnish examples of acidic oxyhydroxides.

In many instances oxyhydroxides may be formed by the removal of water from normal hydroxides by heat. Thus, when the normal aluminium hydroxide, $Al(OH)_3$, is heated, aluminium oxyhydroxide, $AlO(OH)$, results.

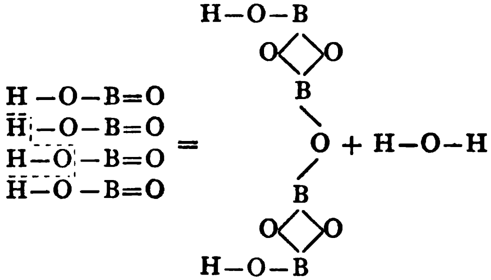


$$Al\left\langle\begin{matrix}O-H\\O-H\\O-H\end{matrix}\right. = Al\left\langle\begin{matrix}=O\\O-H\end{matrix}\right. + H-O-H$$

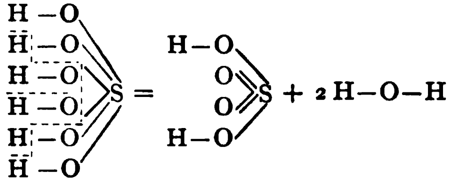
and when orthoboric acid, H_3BO_3, a normal hydroxide, is heated, metaboric acid, HBO_2, an oxyhydroxide, is formed, which by further heating gives tetraboric acid, $H_2B_4O_7$, another oxyhydroxide.



$$\left.\begin{matrix}H-O\\H-O\\H-O\end{matrix}\right\rangle B = \left.\begin{matrix}O=\\H-O\end{matrix}\right\rangle B + H-O-H$$

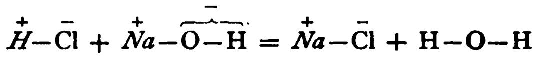


The ordinary sulphuric acid, H_2SO_4, is by constitution an oxyhydroxide which may be considered to be derived by removal of water from a normal hydroxide, H_6SO_6, which, there is reason to believe, exists in suitably concentrated solutions of sulphuric acid in water.



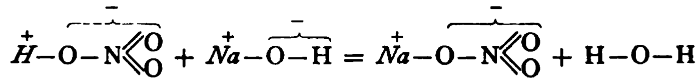
Equations Representing the Formation of Salts.

Graphic symbols may be employed to advantage in representing the part played by the ions in the formation of salts. Thus, we represent the action of hydrochloric acid, HCl, upon sodium hydroxide, NaOH, to form sodium chloride, NaCl, by the equation,



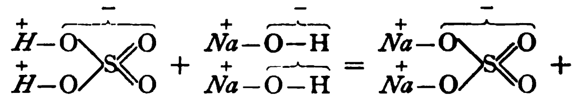
$$\overset{+}{H}-\overset{-}{\mathrm{Cl}} + \overset{+}{Na}-\overbrace{\mathrm{O-H}}^{-} = \overset{+}{Na}-\overset{-}{\mathrm{Cl}} + \mathrm{H-O-H}$$

and the action of nitric acid, HNO_3, upon sodium hydroxide, NaOH, to form sodium nitrate, $NaNO_3$, by the equation,



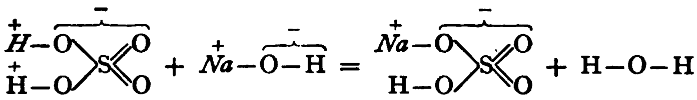
$$\overset{+}{H}-\overbrace{\mathrm{O-N}\begin{smallmatrix}\mathrm{O}\\ \mathrm{O}\end{smallmatrix}}^{-} + \overset{+}{Na}-\overbrace{\mathrm{O-H}}^{-} = \overset{+}{Na}-\overbrace{\mathrm{O-N}\begin{smallmatrix}\mathrm{O}\\ \mathrm{O}\end{smallmatrix}}^{-} + \mathrm{H-O-H}$$

So also we may represent the action of sulphuric acid, H_2SO_4, upon sodium hydroxide, NaOH, to form neutral sodium sulphate, Na_2SO_4, by the equation,

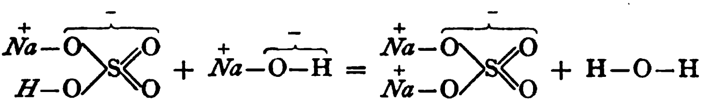


$$\overbrace{\begin{matrix}\overset{+}{H}-\mathrm{O}\\ \overset{+}{H}-\mathrm{O}\end{matrix}>\mathrm{S}<\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}}^{-} + \begin{matrix}\overset{+}{Na}-\overbrace{\mathrm{O-H}}^{-}\\ \overset{+}{Na}-\overbrace{\mathrm{O-H}}^{-}\end{matrix} = \overbrace{\begin{matrix}\overset{+}{Na}-\mathrm{O}\\ \overset{+}{Na}-\mathrm{O}\end{matrix}>\mathrm{S}<\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}}^{-} + \begin{matrix}\mathrm{H-O-H}\\ \mathrm{H-O-H}\end{matrix}$$

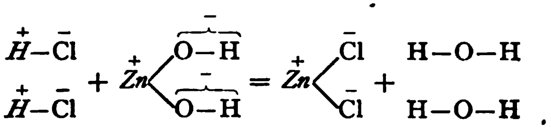
and the reaction of the same substances to form acidic sodium hydrogen sulphate, $NaHSO_4$, by the equation,

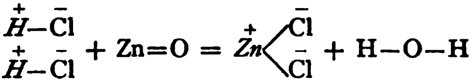


We may also represent graphically the action of sodium hydroxide, NaOH, upon the acidic sodium hydrogen sulphate, $NaHSO_4$, to form neutral sodium sulphate, Na_2SO_4

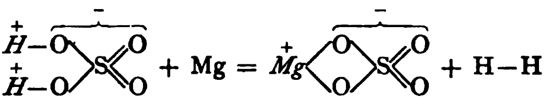


The formation of zinc chloride, $ZnCl_2$, by the interaction of hydrochloric acid, HCl, with zinc hydroxide, $Zn(OH)_2$, and with zinc oxide, ZnO, is shown in the equations,

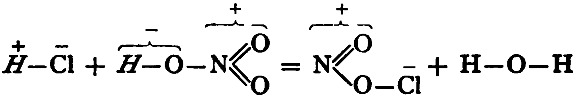




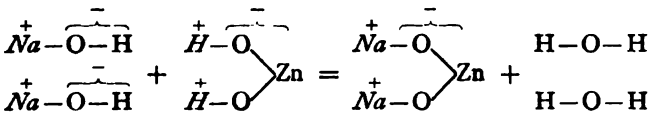
The formation of magnesium sulphate, $MgSO_4$, by the action of sulphuric acid, H_2SO_4, upon magnesium, appears in the equation,



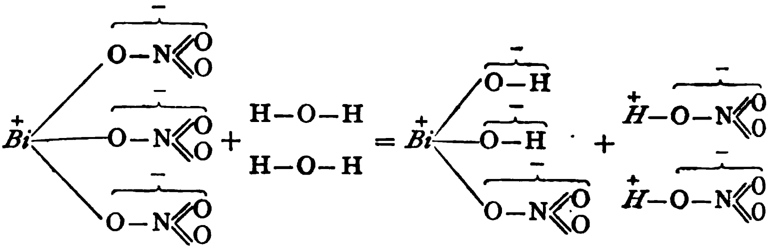
The interaction of hydrochloric acid, HCl, and nitric acid, HNO_3, now appears as



while that between sodium hydroxide, NaOH, and zinc hydroxide, $Zn(OH)_2$, appears in the equation,



The formation of the basic bismuth hydroxynitrate, $Bi(OH)_2NO_3$, by the action of water upon neutral bismuth nitrate, $Bi(NO_3)_3$, may be followed in the equation,

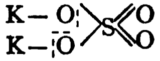


Basicity of Acids, and Acidity of Bases. *An examination of the graphic symbols of acids and bases shows at once the basicity of the acids and the acidity of the bases.* An acid such as hydrochloric acid, $\overset{+}{H}\overset{-}{Cl}$, or nitric acid, $\overset{+}{H}\overbrace{NO_3}^{-}$, with one hydrogen-ion in the true or ideal molecule, is a monobasic acid; while acids which, like sulphuric acid, $\overset{+}{H_2}\overbrace{SO_4}^{-}$, contain two hydrogen-ions, are dibasic acids. Similarly, boric acid, $\overset{+}{H_3}\overbrace{BO_3}^{-}$, is tribasic, and orthosilicic acid, $\overset{+}{H_4}\overbrace{SiO_4}^{-}$ is tetrabasic. In like manner, sodium hydroxide, $\overset{+}{Na}\overbrace{OH}^{-}$, and other basic hydroxides containing one hydroxyl-ion in the molecule, are monacidic bases; calcium hydroxide, $\overset{+}{Ca}(\overbrace{OH}^{-})_2$, and other similar bases are diacidic; while aluminium hydroxide, $\overset{+}{Al}\overbrace{(OH)_3}^{-}$, when acting like a base, is triacidic.

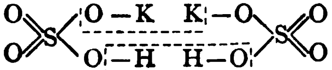
It may be readily observed that with a monobasic acid a monacidic base may form only one salt, and that a neutral salt; while with a dibasic acid a monacidic base may form two salts — a neutral salt and one acidic salt; and with a tribasic acid a monacidic base may form three salts,— one neutral salt and two acidic salts. Corresponding relations between dibasic acids and diacidic bases, and between other polybasic acids and polyacidic bases become apparent upon examination.

Proportional Composition of Salts. *Graphic symbols show clearly the proportions of basic oxide, acidic oxide, and water present in the molecule of a salt.* An ideal molecule of neutral potassium sulphate,

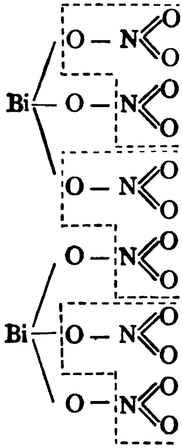
K_2SO_4, contains one molecule of potassium oxide, K_2O, and one molecule of sulphur trioxide, SO_3, as shown in the symbol,



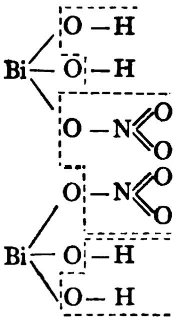
and two ideal molecules of acidic potassium hydrogen sulphate, $KHSO_4$, contain one molecule of potassium oxide, K_2O, two molecules of sulphur trioxide, SO_3, and one molecule of water, H_2O.



Two ideal molecules of neutral bismuth nitrate, $Bi(NO_3)_3$, contain one of bismuth oxide, Bi_2O_3, and three of nitrogen pentoxide, N_2O_5,

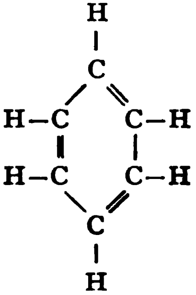


and two ideal molecules of basic bismuth hydroxynitrate, $Bi(OH)_2NO_3$, contain one molecule of bismuth oxide, Bi_2O_3, one molecule of nitrogen pentoxide, N_2O_5, and two molecules of water, H_2O.



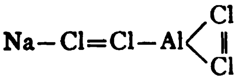
Polymerization of Molecules. Besides the relations of structure involving mass-units within a molecule, certain compounds of molecules with other molecules demand consideration. We have seen that certain molecules may be regarded as unsaturated. For example, in the case of the molecule of acetylene, $H-C\equiv C-H$, it is possible to make other molecules by addition of other mass-units, such as chlorine, bromine, or hydrogen. It is equally possible to *polymerize* acetylene, making three molecules combine to form benzene, C_6H_6, which we may represent by the symbol,

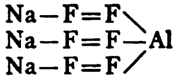
Acetylene.

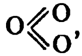


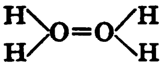
In thus combining molecules of acetylene with one another, use has been made of residual or unused valences of the carbon mass-units.

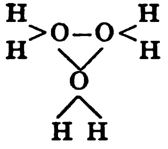
Double Salts. It has been proposed to explain the formation of the so-called *double salts*, by assuming the existence of residual valences in the molecules involved. The molecules of the double chloride of aluminium and sodium, $NaCl.AlCl_3$, and of the double fluoride of aluminium and sodium, $3NaF.AlF_3$, may be represented by assuming the polyvalence of the mass-units of chlorine and fluorine, as shown in the symbols,

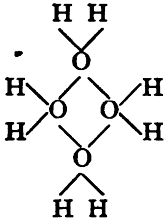




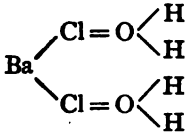
Water of Crystallization. In similar manner, the attachment of water of crystallization in many salts may be attributed to the development of residual valences in the oxygen mass-unit of the water molecule. Thus we have reason to believe that the molecule of liquid water is to be regarded as a polymerized form of the molecule of gaseous water, and such polymerization may easily be represented if we are willing to assume quadrivalence of the oxygen mass-unit. If we give to oxygen a possible valence of four, then ozone, O_3, may be represented by the symbol,  $O\begin{smallmatrix}\diagup O\\ \diagdown O\end{smallmatrix}$, and water in various conditions of polymerization may be represented by the symbols,



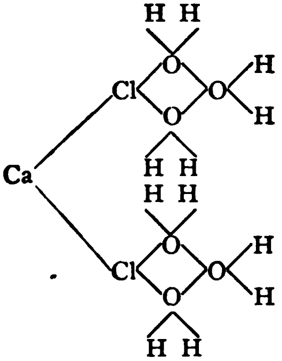




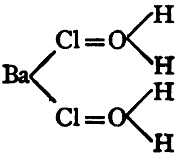
The representation of the attachment of any number of simple water molecules, or polymerized groups of water molecules, to a molecule containing oxygen or other polyvalent mass-unit, may then be a simple matter. For hydrous barium chloride, $BaCl_2 . 2 H_2O$, we may then have the symbol,



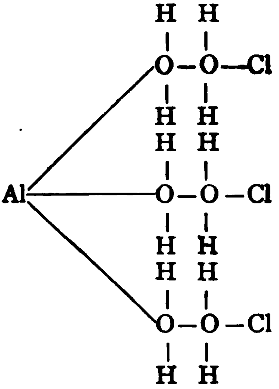
and for the hydrous calcium chloride, $CaCl_2 . 6 H_2O$, we may have the symbol,



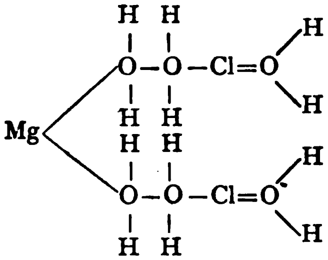
Moreover, the more or less close relation of water of crystallization to the molecules may be indicated by the position of attachment. Thus the molecule of the hydrous crystallized $BaCl_2 . 2 H_2O$, easily dehydrated without loss of chlorine by hydrolysis, may be represented by the symbol,



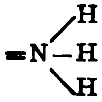
while in the case of hydrous aluminium chloride, $AlCl_3 . 6 H_2O$, from which no water may be expelled without hydrolytic decomposition of the salt, the peculiar relation of the water may be brought out by the symbol,



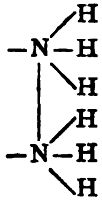
Other hydrous salts, from which a part of the water may be driven without hydrolytic decomposition, while a part is involved in hydrolysis, may be similarly represented, as in the case of magnesium chloride $MgCl_2 . 6 H_2O$,



Ammonia Compounds. The combination of ammonia molecules with the molecules of certain salts, for example, copper sulphate, $CuSO_4$, may be similarly attributed to the satisfaction of residual valences in the nitrogen mass-units, as shown in the symbols,



and



Electrical Charges of Gram-mass-units.

Now let us look once more at the electrical relations of elements taking part in chemical reactions. We have seen that the electrical equivalents of elements, — those weights of substances which are associated in a chemical reaction with the development or conveyance of the same quantities of electricity, — are identical with the chemical equivalents taking part in the reaction. When we experiment with gram-equivalents of the elements, we find that 1 gram-equivalent of oxygen or of any other element requires for its separation in electrolysis nearly 193,000 coulombs of electricity. Knowing the relation of the mass-unit weights of the elements to their respective equivalents, we may calculate the electrical charge in coulombs which is carried in electrolysis by 1 gram-mass-unit of each of the elements.

In the following table appear the electrical charges carried by gram-mass-units of some elements, calculated from the equivalents, and the charge of a gram-equivalent, together with the relation of the gram-mass-unit charges to the respective valences of the elements:

Electrical Charges and Valences of Mass-units

Element	Equivalent Oxygen/16	Charge of One Gram-equivalent Coulombs	Mass-unit Weight Oxygen/16	Charge of One Gram-mass unit Coulombs	Valence H=I	Charge of Mass-unit ÷ Valence Coulombs
Aluminium	18.07	193000	27.1	289320	III	96500
Bismuth	139.0	193000	208.5	289320	III	96500
Chlorine	70.90	193000	35.45	96440	I	96500
Copper	63.6	193000	63.6	192880	II	96500
	127.2	193000	63.6	96440	I	96500
Hydrogen	2.015	193000	1.0075	96440	I	96500
Oxygen	16.00	193000	16.00	192880	II	96500
Silver	215.86	193000	107.93	96440	I	96500
Zinc	65.4	193000	65.4	192880	II	96500

From these relations it appears that the charge of 1 gram-mass-unit in coulombs varies for different elements according to the valence of the mass-units of these elements, and that the charge obtained by dividing the gram-mass-unit charge of each element by the valence of the element is in every case 96,500 coulombs. Since gram-mass-units of different elements represent equal numbers of mass-units, it appears that *the valence of an element indicates a number of definite electrical charges associated with the mass-unit of the element; and the graphic symbol of an element or compound serves, therefore, to indicate the number of the electrical charges associated with the individual mass-units, or with the ions constituting the compound.*

CHAPTER XV

THEORY

Inductions. THUS far we have been concerned with observed facts and simple inductions from observations. What we have seen of chemical change has led us to infer the existence of certain forms of matter, simple, undecomposable by the processes of analysis, and therefore called the *chemical elements*. Investigation of the properties and relations of some of these elementary forms of matter and of the compounds which they form has resulted in generalizations which affirm the *constancy of composition* of individual substances, the interaction of substances in *definite proportions* to form a given substance, and in *multiple proportions* of these same definite proportions to form more than one substance consisting of the same elements in varied amount.

We have found it convenient to arrange a system of *chemical equivalents*, *electrical equivalents*, and *thermal equivalents* which express the relative weights of elements associated definitely and essentially in chemical, electrical, and thermal phenomena. Inferring from the phenomena that these equivalents stand for proportionate numbers of masses which act as units in chemical action, we have derived the idea of *mass-units* of the elements, and the conception of *molecules* consisting of one or more elementary mass-units, and constituting the active mass in which the properties of the substance, elementary or compound, reside.

We have thus been able to construct a system in which substances, elementary or compound, may be arranged and discussed without the assumption of any hypothesis as to the mechanical nature and constitution of matter. So far as observations have been accurate, the record of facts will stand; the correctness of our inferences may be assumed so long as they remain in harmony with new facts as they develop.

Hypothesis. To account for observed phenomena it has been found advantageous to form a *hypothesis*, or provisional theory, of matter, which, although not susceptible of direct proof, nevertheless is in accord with the truth so far as it is known, and serves as a stimulus to investigation and as a basis for the coördination of new discoveries.

Conception of Matter. The conception of matter as made up of indivisible particles is a hypothesis which goes back through the Romans and Greeks to the philosophers of ancient India; but the epoch-making idea that ultimate particles of matter have definite weights, every elementary substance consisting of particles of the same kind and characteristic weight, was first advanced by John Dalton in 1803. In accordance with this idea the name given by the ancient philosophers to their indivisible particles may be applied to the individual masses of definite weight of which we have had evidence in chemical action.

Atoms. The mass-units may be called *atoms*. The theory of matter which assumes the existence of the mass-units as individual particles is the *atomic theory*. *According to this atomic theory, elements are made up of atoms of the same kind and weight, and compounds are made up of atoms of different kinds and weights. In the chemical sense the atom is, therefore, something that has not been divided — the smallest mass of a chemical element which enters into any known chemical compound.* With ideas of indivisibility, indestructibility, absolute hardness, or with any of the abstract conceptions which for the philosopher cluster about the word *atom*, the chemist has nothing to do. To him *the atom is simply the unit of chemical action — the individual mass of matter which undergoes no change in ordinary chemical reactions.*

Radio-activity. Certain simple relations which we shall discuss later between the atomic weights of some elements, as well as the structure of their spectra, suggest, however, that atoms may be complex, and the phenomena of *radio-activity* give rise to the idea that changes are possible in the atoms of radio-active substances. As early as 1815 Prout advanced the view that the atoms of chemical elements other than hydrogen are complexes of hydrogen; but later and better determination of atomic weights having shown plainly that all atomic weights are not simple whole multiples of the atomic weight of hydrogen, Dumas suggested that the primordial atom of which all other atoms might be complexes might have one half or one fourth the mass of the hydrogen atom.

Electrons. Very recently J. J. Thomson has derived from the consideration of the electrical relations of matter the idea that the atoms of the elements are built up of simpler systems of primordial atoms and *electrons*, or corpuscles of negative electricity, the character of the atoms as positive or negative being determined by their tendency to lose or gain electrons, and the valence of the atoms depending upon the numbers of electrons which may be lost or gained.

Given the conception of the atom, the relative weights which represent *thermal equivalents* stand for equal numbers of atoms, and the weights which represent *chemical and electrical equivalents* stand either for equal numbers of atoms or for simple multiples of equal numbers of atoms. The law of *definite proportions* finds explanation in the fact that definite numbers of atoms of definite kinds combine, and the law of *multiple proportions* is accounted for in the combination of different simply related numbers of atoms of the same kind with definite numbers of atoms of other kinds. The *molecule*, the smallest mass of matter in which the properties of a substance reside, is either an atom or an aggregation of atoms which acts as a unit so long as the substance retains its identity. The *ion* is an atom or group of atoms which moves from compound to compound.

Atomic Weights. Obviously our system of *symbols* adapted to indicate mass-units and the aggregations of mass-units in molecules may be applied without change to atoms and aggregations of atoms. If we make the atom of oxygen weigh 16, the numbers which represent the atoms of other elements will be expressed by their mass-unit weights. When Dalton introduced the atomic theory into the consideration of chemical phenomena, the atomic weight of hydrogen, the lightest of the elements, was taken as 1, and other elements were given atomic weights proportionate to chosen equivalents. If we take the atomic weight of hydrogen as 1 instead of 1.0075 and make it the basis of a system of atomic weights, determined by the ratios of the mass-unit weights, the atomic weight of oxygen will be 15.88, the atomic weight of nitrogen 13.93, and the atomic weights of other elements will be proportionately varied from the mass-unit weight referred to oxygen as 16. Such a system of atomic weights as this has the historical precedence and is preferred by some. On the other hand, the practical determination of equivalents is generally made by direct reference to oxygen in oxygen compounds rather than to hydrogen in hydrogen compounds, and for this reason the atomic weight of oxygen is the natural basis of atomic weights, and it is convenient to take this as 16 rather than as 15.88. For purposes of calculation either system of atomic weights will answer equally as well as the other, and at the present time it is customary to give both systems, as shown in the table:

TABLE OF ATOMIC WEIGHTS

		O = 16	H = 1			O = 16	H = 1
Aluminium	Al	27.1	26.9	Neodymium	Nd	143.6	142.5
Antimony	Sb	120.2	119.3	Neon	Ne	20.	19.9
Argon	Ar	39.9	39.6	Nickel	Ni	58.7	58.3
Arsenic	As	75.0	74.4	Nitrogen	N	14.04	13.93
Barium	Ba	137.4	136.4	Osmium	Os	191.	189.6
Bismuth	Bi	208.5	206.9	Oxygen	O	*16.00*	15.88
Boron	B	11.	10.9	Palladium	Pd	106.5	105.7
Bromine	Br	79.96	79.36	Phosphorus	P	31.0	30.77
Cadmium	Cd	112.4	111.6	Platinum	Pt	194.8	193.3
Caesium	Cs	132.9	131.9	Potassium	K	39.15	38.86
Calcium	Ca	40.1	39.8	Praseodymium	Pr	140.5	139.4
Carbon	C	12.00	11.91	Radium	Ra	225.	223.3
Cerium	Ce	140.25	139.2	Rhodium	Rh	103.0	102.2
Chlorine	Cl	35.45	35.18	Rubidium	Rb	85.5	84.9
Chromium	Cr	52.1	51.7	Ruthenium	Ru	101.7	100.9
Cobalt	Co	59.0	58.56	Samarium	Sm	150.3	149.2
Columbium	Cb	94.	93.3	Scandium	Sc	44.1	43.8
Copper	Cu	63.6	63.1	Selenium	Se	79.2	78.6
Erbium	Er	166.	164.8	Silicon	Si	28.4	28.2
Fluorine	F	19.	18.9	Silver	Ag	107.93	107.12
Gadolinium	Gd	156.	155.	Sodium	Na	23.05	22.88
Gallium	Ga	70.	69.5	Strontium	Sr	87.6	86.94
Germanium	Ge	72.5	71.9	Sulphur	S	32.06	31.83
Glucinum	Gl	9.1	9.03	Tantalum	Ta	183.	181.6
Gold	Au	197.2	195.7	Tellurium	Te	127.6	126.6
Helium	He	4.	4.	Terbium	Tb	160.	158.8
Hydrogen	H	1.008*	*1.000*	Thallium	Tl	204.1	202.6
Indium	In	115.	114.1	Thorium	Th	232.5	230.8
Iodine	I	126.97	126.01	Thulium	Tm	171.	169.7
Iridium	Ir	193.0	191.5	Tin	Sn	119.0	118.1
Iron	Fe	55.9	55.5	Titanium	Ti	48.1	47.7
Krypton	Kr	81.8	81.2	Tungsten	W	184.	182.6
Lanthanum	La	138.9	137.9	Uranium	U	238.5	236.7
Lead	Pb	206.9	205.35	Vanadium	V	51.2	50.8
Lithium	Li	7.03	6.98	Xenon	Xe	128.	127.
Magnesium	Mg	24.36	24.18	Ytterbium	Yb	173.0	171.7
Manganese	Mn	55.0	54.6	Yttrium	Yt	89.0	88.3
Mercury	Hg	200.0	198.5	Zinc	Zn	65.4	64.9
Molybdenum	Mo	96.0	95.3	Zirconium	Zr	90.6	89.9

* More accurately 1.0075.

Relations of Atoms in Space. If we accept the idea of atoms, and of molecules composed of atoms, the graphic symbols of molecules suggest at once relations in space of the atoms which compose the molecules. In the symbol of methane, CH_4, for example, there is suggested the idea of a central carbon atom, C, surrounded by four hydrogen atoms. If these four hydrogen atoms all sustain the same relation to the carbon, as seems to be the case, we may conceive of the hydrogen atoms as arranged symmetrically with reference to the central carbon atom. Putting the carbon atom at the center of a sphere, the hydrogen atoms fall very naturally in the periphery of the sphere in such manner that the lines joining them form the edges of a tetrahedron inscribed in the sphere at the center of which is the carbon atom.

Isomerism. This idea of arrangement in space, the development of which to a working hypothesis we owe to Van't Hoff, makes it possible to express graphically certain very interesting and peculiar relations of *isomerism.* We have already noted a kind of isomerism which depends upon the mutual relations of the atoms of a molecule as evidenced in chemical reaction. There seems to be also a kind of *physical isomerism* of compounds which have closely similar chemical relations to other substances, but which differ markedly in their behavior toward that modification of light which we call *polarized light,* turning the plane of polarization to the right or to the left.

Asymmetric Carbon Atoms. Many compounds may be formed by replacing the hydrogen atoms of methane by other univalent atoms or radicals, but so long as these four atoms or radicals are not all different, the structure of the molecule thus formed will depend simply upon the kind and number of replacements, and not at all upon the position of the replacement. Thus, the symbols $CR_1R_1R_1R_1$, $CR_1R_1R_1R_2$, $CR_1R_1R_2R_2$, $CR_1R_1R_2R_3$, will each be represented by a simple tetrahedron, but for the symbol $CR_1R_2R_3R_4$ either of two tetrahedra will be a possibility depending upon the arrangement of the atoms or radicals R_1, R_2, R_3, and R_4. Such tetrahedra, shown in the figures, are not identical and cannot be made to coincide by any movement of either tetrahedron

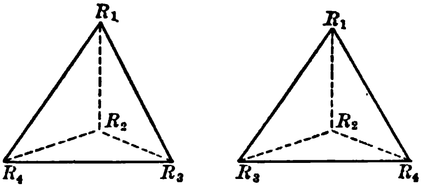


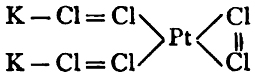
FIG. 45. — Asymmetric Carbon Atom.

as a whole, but bear to one another a right and left relation, like that of the right and the left hand. The carbon atom about which the four different atoms or radicals are grouped is said to be an *asymmetric* carbon atom.

Tartaric Acids. Now, it sometimes happens that a compound of carbon rotates the plane of polarization to the right, while a compound of identical composition and action rotates it to the left, and it appears that the molecules of all such compounds contain at least one asymmetric carbon atom, about which are grouped four different radicals. Such compounds are *physical isomers* and may be represented by right-handed and by left-handed tetrahedra. In some cases more than one carbon atom within the molecule is asymmetric, and in such cases the possibilities of physical isomerism are increased. We know, for example, four isomers or kinds of tartaric acid differing in the action upon polarized light: the dextrorotatory or right-handed tartaric acid, which turns the plane of polarization of light to the right; the levorotatory or left-handed tartaric acid, which turns the plane of polarization to the left; the neutral tartaric acid, also known as racemic acid, which does not affect the plane of polarization of light, but which may be separated by appropriate means into the dextrorotatory and levorotatory forms; and a fourth neutral form, known as inactive tartaric acid which, like the neutral tartaric acid, does not affect the plane of polarization of light, but, unlike the neutral tartaric acid, is not separable into the dextrorotatory and the levorotatory forms. It is noteworthy also in the case of the tartaric acids that the arrangement of certain faces upon the crystals of the dextrorotatory and levorotatory forms is right-handed or left-handed, respectively. This **Stereo-isomerism.** relationship of compounds of identical composition and action, which may be expressed by the spatial relations of the atoms in the molecules, is known as the *stereo-isomerism* of the compounds.

Nucleus of Compounds. An explanation of the constitution of compounds of molecules with molecules, such as the so-called double salts, salts containing water of crystallization, or ammonia complexes, has been attempted by Werner in an extension of the conception of the spatial relations of atoms and groups of atoms forming a complex with a central atom. Upon the valence of the central atom depends the valence of the complex. The central atom and the associated atoms or groups together constitute the *nucleus*, the character of which depends upon the coördinated elements or groups. For many such nuclei the limiting number of atoms or groups associated with the central atom is six; for others it is four.

Upon this hypothesis the compound K_2PtCl_6, sometimes called a double salt of potassium chloride and platinum tetrachloride, $2\,KCl \cdot PtCl_4$, and sometimes considered to be a potassium salt of chlorplatinic acid,



is to be regarded as the combination of two outlying atoms of potassium with a nucleus, $PtCl_6$, and to be represented spatially by placing the platinum atom at the center of an octahedron, with the chlorine atoms at the solid angles, which thus constitutes a nucleus outside of which the potassium atoms lie.

In the ordinary reactions of these compounds, and of compounds similarly put together, the nucleus, in this case $\overset{-}{PtCl_6}$, acts as one ion, while the outlying atoms or groups, in this case $2\,\overset{+}{K}$, are ions of sign unlike that of the nucleus.

When water molecules are the associated groups of the nucleus, they may constitute a part of the nucleus ion. Thus, according to Werner's hypothesis, hydrous cobalt chloride, $CoCl_2 \cdot 6\,H_2O$, is to be written $Co(H_2O)_6 \cdot Cl_2$, and when this salt enters into reaction in water solution, the ions are $\overset{+}{Co(H_2O)_6}$ and $2\,\overset{-}{Cl}$. Represented by diagram, the cobalt atom is at the center of the octahedron, with a molecule of water at each solid angle, while the chlorine atoms are outlying.

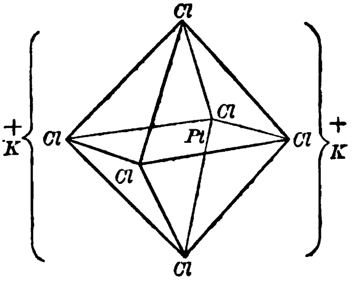


FIG. 46. — Nucleus Structure of Potassium Chlorplatinate.

Many ammonia compounds, cyanides, nitrites, and other compounds, may be referred to the octahedral nucleus; for certain other compounds a tetrahedral nucleus has been suggested.

The conception of the molecule as an atom or aggregation of atoms acting as a unit, and of matter as made up of such units, is quite in accord with what we observe in certain physical phenomena. It is

The Atoms in Solids, Liquids, and Gases.

not possible to regard matter as continuous and homogeneous, or jellylike, for, if it were so, we have no reasonable explanation for phenomena like the dispersion of rays of light by refracting media, some manifestations of contact electricity, the properties of liquid films, and the behavior of gaseous substances when subjected to changing temperatures and pressures. But if matter is not homogeneous, or jellylike, the idea that the molecules of matter are particles is most plausible.

Now, if we endow these molecules with motion, make the rapidity of the motion proportional to temperature, that is, faster as the body gets hotter and slower as it gets cooler, several interesting conclusions follow. The rigidity of *solid* bodies now seems to show that in them the molecules do not move far from the positions in which they may be at any instant; the mobility and power of *liquids* to flow or diffuse would indicate that the molecules are free to move in any direction without necessarily returning to their original positions; while the tendency of *gases* to escape from containing vessels unless restrained on all sides would seem to show greater freedom of motion of the molecules. According to the molecular theory, we find in the degree of separation of the molecules the explanation of the enormous expansion which takes place when a liquid becomes gas, and of the great condensation which is observed when a gas is liquefied. Furthermore, the regularity of expansion and contraction of a gas under changing conditions of temperature and pressure find similar explanation. Liquid hydrogen expands about 780 times in becoming gaseous at 0° and 760 mm., gaseous hydrogen under unchanged pressure gains or loses $\frac{1}{273}$ of its volume at 0° for every degree of increase or decrease respectively of temperature, and at a constant temperature its volume varies inversely as the pressure put upon it, because in these changes of physical condition the average distance of the molecules from one another becomes greater or less.

Kinetic Theory of Gases.

The relations of molecular motion to phenomena are best studied in gaseous substances, and were first developed by Bernoulli in 1740, and by Krönig and Clausius, about 1856, and are expressed in the *Kinetic Theory of Gases*.

Thus, if we suppose the structure of perfect gases to be such that, (1) the gas is made up of molecules moving with a velocity proportional to the temperature, that (2) the number of molecules in any mass of gas that can be handled experimentally may be regarded as inconceivably large, while (3) the dimensions of the molecules are small in comparison with their average distance apart, and (4) the time during which any molecule is in close proximity to any other molecule is very short when compared with the time during which it is remote from any other molecule, we may find by the principles of mechanics an expression for the pressure per unit area of any perfect gas in terms of the weight of a single molecule, the number of molecules, the average velocity of the molecules, and the volume of the gas.

Let p be the pressure of a gas, N the number of molecules in 1 cm.^{3}, m the weight of each molecule in grams, ρ the specific gravity to water, and V the average velocity of the molecules in centimeters in a second, all within a rectangular box having the edges a, b, c. When a molecule strikes a wall, for example, the wall bc, it will rebound with the same velocity, in the average, with which it impinged upon the wall, and the momentum, or motion, of the molecule is reversed; from $+mV$ it becomes $-mV$, and the total change of motion is $2\,mV$.

Now the rate at which the motion is changed is the measure of the force exerted by the wall, and $\frac{2\,mV}{t}$ therefore measures the average force exerted by the wall upon a molecule when t represents the duration of the action in seconds. The number of impacts in a second upon the wall is assumed to be infinitely great, and the total force exerted by the wall will be constant and equal to the product of the number of impacts into $\frac{2\,mV}{t}$, the force exerted upon a molecule during a single impact.

It is fair to assume, provisionally, for the purpose of the demonstration, that all the molecules are moving with the average velocity, and that by the resolution of motion $\frac{1}{3}$ of all the molecules may be regarded as moving in lines parallel to one of the edges a, b, c. Now let us see how many molecules strike the side bc in a given time. Consider the case of a molecule just leaving bc in the direction of the edge a. This molecule will have to traverse a in both directions before it strikes bc, and then will have to again traverse a in both directions before it makes a second impact on bc. That is, $\frac{V}{2\,a}$ will show the number of times the molecule will strike bc in a second, and $\frac{Vt}{2\,a}$ will give the number of impacts in the time t. Now, the whole number of molecules in the box is $Nabc$, and $\frac{1}{3}$ of them, or $\frac{1}{3}\,Nabc$, are in motion so that they strike the side bc. So the expression,

$$\tfrac{1}{3}\,Nabc \times \frac{Vt}{2\,a} = \tfrac{1}{6}\,NbcVt$$

gives the number of impacts on bc in the time t. The whole constant force exerted by the wall, the product of the number of impacts by the force exerted by the wall upon each molecule, will be given by the expression,

$$\tfrac{1}{6}\, NbcVt \times \frac{2\,mV}{t} = \tfrac{1}{3}\, NbcmV^2,$$

which also gives the total pressure upon the wall, since this is equal to the force exerted by the wall.

The total pressure upon the wall divided by the number of square centimeters of area on the wall will give the pressure upon 1 cm.^{2} of surface, which is what we mean ordinarily when we speak of the pressure of a gas. So we have

$$p = \frac{\tfrac{1}{3}\, NbcmV^2}{bc} = \tfrac{1}{3}\, NmV^2,$$

and since the specific gravity of the gas to water is equal to the product of the number of molecules in 1 cm.^{3} by the weight of each molecule in grams,

$$\rho = Nm,$$

it follows that

$$p = \tfrac{1}{3}\, \rho V^2.$$

For any other pressure, p', the temperature being constant and the velocity of the molecules the same (a condition obtained, for example, by allowing the gas to expand into a vacuum when, as experiment shows, there is no change of temperature), we have, when ρ' is the new specific gravity,

$$p' = \tfrac{1}{3}\, \rho' V^2,$$

whence, if v and v' represent the volumes of the same weight of gas under the pressures p and p',

$$\begin{aligned} p : p' &= \tfrac{1}{3}\, \rho V^2 : \tfrac{1}{3}\, \rho' V^2 \\ &= \rho : \rho' = v' : v. \end{aligned}$$

Boyle's Law. That is, the volume of a gas varies inversely with the pressure put upon it, the temperature remaining constant, as stated in the *Law of Boyle*.

For two conditions of a constant volume, v, of gas corresponding to two pressures, p, p', and two temperatures, t, t', we have

$$p = \tfrac{1}{3}\, mNV^2$$

$$p' = \tfrac{1}{3}\, mNV'^2$$

whence, since N is constant, the number of molecules being unchanged,

$$p : p' = mV^2 : mV'^2$$

But, as Maxwell has shown, two temperatures, T, T', measured on the absolute scale, are proportionate to the kinetic energy of the molecules, or,

$$T : T' = \tfrac{1}{2}\, mV^2 : \tfrac{1}{2}\, mV'^2$$

so that

$$p : p' = T : T'$$

If, now, we take the gas at the volume v, and the pressure p', and absolute temperature T', and allow it to expand into a vacuous space to the volume v' until p' takes the value p while T' remains constant, the new volume V' may be found by the Law of Boyle. Thus,

$$v : v' = p : p'$$

Whence $$v : v' = T : T'.$$

Charles' Law. That is, under constant pressure, the volume of a gas varies directly as its absolute temperature, as stated in the *Law of Charles.*

Furthermore, for equal volumes of two gases under the same pressure, p, we have the expression,

$$p = \frac{1}{3} mNV^2 = \frac{1}{3} m'N'V'^2$$

If, now, the temperature be the same, the kinetic energy of the molecules of the two masses will be the same, and

$$\frac{1}{2} mV^2 = \frac{1}{2} m'V'^2$$

Whence, $$N = N'.$$

Avogadro's Law. That is, equal volumes of gases under the same conditions of temperature and pressure contain the same number of molecules, as stated in the *Law of Avogadro.*

So it appears that the laws of Boyle, Charles, and Avogadro follow directly from the postulates of the kinetic theory of gases.

Velocity of Molecules. Incidentally, we may note that it is also possible, by means of the equation given above, defining the pressure of a gas in terms of the molecular weight, velocity, and number of molecules, to deduce approximately the *molecular velocity* when the pressure is known, and when the product of the molecular weight into the number of molecules, or the density, is also known; but Maxwell has pointed out that the assumption that all the molecules have the same velocity introduces an error of about $\frac{1}{13}$ of the whole value. Making this correction, the results of such calculations appear as shown in the table:

Average Velocities of Gas Molecules

	Centimeters in a Second		Centimeters in a Second
Hydrogen . . .	169800	Chlorine	28600
Hydrogen oxide .	56600	Bromine	19000
Nitrogen	45300	Mercury	16900
Oxygen	42500	Iodine	15100
Carbon dioxide . .	36100		

We may note, also, as a matter of curiosity, that for finding out the numbers of molecules in a mass of gas, as well as the sizes and weights of the molecules of different gaseous substances, many ingenious methods have been derived by Lord Kelvin, J. J. Thomson, Nernst, and others. The number of molecules in 1 cm.^{3} of any perfect gas at 0° and 760 mm. has been estimated to be approximately 21,000,000,000,000,000,000. The sizes of the molecules of different individual substances appear, though not exactly equal, to be of the same order of magnitude, those of carbon dioxide and hydrogen being found to be 0.000,000,018 cm. and 0.000,000,014 cm. in diameter, respectively. It has been estimated that a molecule of hydrogen weighs 0.000,000,000,000,000,000,000,004,27 grm., an amount which may be ten times too large or ten times too small.

Dissociation of Molecules in Solution. In our study of the osmotic pressure exerted by substances in solution, and the lowering of the freezing point and rise of the boiling point of a solvent under the action of a solute, we noted that *just as some gaseous molecules appear to dissociate into simple aggregations of mass-units or atoms at high temperatures, so also the molecules of electrolytes appear to dissociate in solution to form a larger number of active units.*

Specific Gravity. Similar relations have been observed in regard to other phenomena of solution. This, in 1874, Valson, pointing out that the *specific gravity* of the solution of certain salts, electrolytes, is made up of two values or "moduli," the one depending upon the nature of the positive ion and the other upon the nature of the negative ion of the salt, drew the conclusion that the molecules of the salts with which he experimented were resolved into parts in solution.

Volume. Ostwald's study of the *change of volume* produced upon neutralizing by bases gram-equivalents of acids in a kilogram of water is suggestive of a similar conclusion. Ostwald worked with nineteen acids and the three bases, sodium hydroxide, potassium hydroxide, and ammonium hydroxide, and found that the difference between the changes of volume consequent upon the neutralization of different bases by a given acid appears to be nearly independent of the nature of the acid; and, similarly, that the difference between the changes in volume accompanying the neutralization of different acids by a given base is nearly independent of the nature of the base. These phenomena also suggest that the molecules of the salts act as if resolved into parts in solution.

Heat of Neutralization. The *heat changes* involved in the neutralization of bases and acids are very noteworthy phenomena of similar character. When, for example, gram-equivalent weights of certain different acids are neutralized in dilute solution by a given base, the heat of neutralization is nearly constant for a considerable series of typical acids, and similarly the heat of neutralization of a given acid is nearly constant for a considerable series of bases. These facts are set forth in the following table:

HEAT OF NEUTRALIZATION IN DILUTE SOLUTION

BASE Grm.-equiv.	ACID Grm.-equiv.	THERMAL CHANGE (Common Calories)
NaOH	HCl	13700
NaOH	HBr	13700
NaOH	HNO_3	13700
NaOH	HI	13800

ACID Grm.-equiv.	BASE Grm.-equiv.	THERMAL CHANGE (Common Calories)
HCl	LiOH	13700
HCl	KOH	13700
HCl	$\frac{1}{2}Ba(OH)_2$	13800
HCl	$\frac{1}{2}Ca(OH)_2$	13900

Hess's law of the thermoneutrality of salt solutions, to the effect that sufficiently dilute solutions of salts mix without thermal change, also suggests the idea that at sufficient dilution the molecules of salts are resolved into parts which remain independent when the solutions are mixed.

Ions and Atoms. In our study of the phenomena of the mutual neutralization of acids and bases with the formation of salts, we were led to see that in such reactions certain parts of compounds move from one combination to another combination, and that such parts prove to be the same parts which move under the influence of the electric current and which were called *ions* by Faraday. We learned to recognize the individuality of the ions and their functions in determining the course of a reaction. When we arrived at the conception of mass-units of the elements, and molecules of elements and compounds made up of mass-units, it became plain that the properties of the compound reside in the molecule and that the ion is represented by a mass-unit or aggregation of mass-units acting as an individual. If we adopt the atomic theory, the molecule in which the properties of the compound reside is made up of atoms, and *the ions are single atoms or individual aggregations of atoms.*

Electrolytic Dissociation or Ionization. The phenomena of salt solutions which we have been discussing—the excessive osmotic pressure and depressions of the freezing point and elevations of the boiling point, Valson's variations of specific gravity, Ostwald's changes of volume by neutralization of base and acid, the heats of neutralization of base and acid, the thermoneutrality of dilute salt solutions—point strongly to the especial activity of the ions of electrolytes in solution. It was to account for the phenomena noted by Van't Hoff in regard to osmotic pressure, the lowering of the freezing point and the rise of the boiling point of solutions, that Arrhenius, in 1887, advanced the hypothesis that *the molecules of an electrolyte tend to dissociate in solution into free, electrically charged parts, which are the ions of chemical action.*

The hypothesis that the molecules of an electrolyte in a solution through which an electric current is passing are dissociated into smaller parts or *ions* carrying the current has long been accepted, as we have seen, in explanation of the phenomena of the electrolytic cell. It has been assumed that the ions move through a solution, the positively charged ion toward the negative pole and the negatively charged ion toward the positive pole, both positive and negative ions being capable of independent existence so long as they hold their charges, but recombining or entering into other reactions with the materials of the poles, or solvents, or other solute, upon surrendering their charges at the poles. Thus, as we have seen, in the electrolysis of hydrogen chloride we have:

$$2\,HCl = 2\,\overset{+}{H} + 2\,\overset{-}{Cl} = H_2 + Cl_2$$

The atoms of hydrogen and of chlorine are here the ions, charged with electricity and serving to carry their charges to the respective poles before they combine to form hydrogen molecules and chlorine molecules, respectively. This idea of the dissociation of molecules into ions during the electrolytic process was proposed by Faraday, and Clausius in 1856 showed that some slight ionization of the molecules of an electrolyte, due, perhaps, to molecular collisions, must, according to the theory of thermodynamics, precede the passage of the current.

The hypothesis of Arrhenius postulates that by the act of solution the molecules of electrolytes are ionized very largely, and at extreme dilution completely; that the conductivity of the solution is proportional to the degree in which the solute is ionized; and that in the process of electrolysis the electric current simply assembles at opposite poles the electrically charged ions already present. For example, according to the theory of Arrhenius, when hydrogen chloride is dissolved in a sufficient amount of water, the molecule HCl is dissociated by the action of water into the oppositely charged ions $\overset{+}{H}$ and $\overset{-}{Cl}$, distributed through the solvent,

$$HCl = \overset{+}{H} + \overset{-}{Cl}$$

and this is the reason why, in working experimentally with dilute solutions of hydrogen chloride, the values found for the osmotic pressure, the depression of freezing point, the decrease in vapor tension and consequent increase in boiling point, are all greater than would be expected if we were dealing with whole molecules HCl as units of action.

Electrical Conductivity of Solutions.

In general, the dissociation of molecules of solutes into ions, as indicated especially by the effects on osmotic pressure, freezing points, and boiling points, increases with the dilution until a maximum effect is reached; and it is noteworthy, also, that the *electrical conductivity* of the solution likewise increases with the degree of dissociation of the dissolved electrolyte, and reaches a maximum when the dilution attains a certain value.

Neutralization of Acids and Bases.

Chemical reaction in solution takes on a new aspect in the light of the theory of electrolytic dissociation. Let us consider, for example, the mutual neutralization of a base and an acid. Sodium hydroxide breaks down in dilute solution according to the theory into the positively charged sodium-ion, $\overset{+}{Na}$, and the negatively charged hydroxyl-ion, $\overset{-}{OH}$, while hydrogen chloride is decomposed into the positive hydrogen-ion, $\overset{+}{H}$, and the negative chlorine-ion, $\overset{-}{Cl}$. Water itself is dissociated so little that we may regard it as practically undissociated. The reaction of sodium hydroxide in dilute solution upon hydrogen chloride will then be expressed:

$$\overset{+}{Na} + \overset{-}{OH} + \overset{+}{H} + \overset{-}{Cl} = \overset{+}{Na} + \overset{-}{Cl} + H_2O$$

which means that, starting with the free ions $\overset{+}{Na}$, $\overset{-}{OH}$, $\overset{+}{H}$, $\overset{-}{Cl}$, the action results in the union of $\overset{+}{H}$ and $\overset{-}{OH}$ to form the un-ionized molecule, H_2O. Similarly, we might write the equation for the neutralization of potassium hydroxide by nitric acid thus:

$$\overset{+}{K} + \overset{-}{OH} + \overset{+}{H} + \overset{-}{NO_3} = \overset{+}{K} + \overset{-}{NO_3} + H_2O$$

In terms of the theory of electrolytic dissociation, therefore, the *mutual neutralization of bases and acids in sufficiently dilute solution consists essentially in the union of the positive hydrogen-ions with the negative hydroxyl-ions, the ions of the metal and of the non-metal group remaining dissociated in the solution until the removal of the solvent permits them to combine to form a salt.*

Now, if this is the real state of the case, the actual chemical change being the same no matter what bases or acids are present, the energy manifested in the neutralization of completely dissociated bases and acids should be the same. The fact is, as we have seen, that the heats of neutralization of certain bases and certain acids prove to be the same whatever be the individuality of the base or acid, and this phenomenon finds explanation in the hypothesis *that the mutual neutralization of a base and an acid in a sufficiently dilute solution is, in every case, simply the formation of un-ionized molecules of water.*

Looking back to our experiments upon the conditions of chemical action, we recall that when, in the establishment of equilibrium between substances in solution, a product insoluble and inactive or volatile is formed, or when water is a product, the formation of such insoluble or volatile product or the formation of inactive water goes on until one or other of the factors involved in the change is exhausted. Volatility will, of course, remove a product from the sphere of action, and the completion of a reaction in which a product is volatile is to be expected. But why should the formation of an insoluble product or the production of water be the determining cause of a complete reaction ? The theory of electrolytic dissociation proposes an explanation in the hypothesis that *the ions alone are concerned in chemical changes in solution, and when by combination of free ions an un-ionized molecule may be formed, whether it be soluble or insoluble, such reaction will proceed until at least one kind of ion is exhausted.*

Thermo-neutrality. Another point which should be touched upon in connection with the theory of electrolytic dissociation has been referred to previously as *Hess's Law of thermoneutrality.* Why is it that, when very dilute solutions of neutral salts are mixed, no heat manifestations are observed ? The answer, according to the theory, is that *neutral salts are dissociated in dilute solution into free ions, which remain free so long as the solution is dilute enough to ionize any possible combination of them.* Thus, KCl becomes $\overset{+}{K}$ and $\overset{-}{Cl}$, and $NaNO$

becomes $\overset{+}{\mathrm{Na}}$ and $\overset{-}{\mathrm{NO}}_3$, in dilute solution. When $\overset{+}{\mathrm{K}} + \overset{-}{\mathrm{Cl}}$ and $\overset{+}{\mathrm{Na}} + \overset{-}{\mathrm{NO}}_3$ are intermixed to form $\overset{+}{\mathrm{K}} + \overset{-}{\mathrm{Cl}} + \overset{+}{\mathrm{Na}} + \overset{-}{\mathrm{NO}}_3$, there should be no thermal change, since the conditions of solution are such that every salt, KCl, KNO_3, NaCl, $NaNO_3$, which under the conditions might be formed from these ions would be dissociated into ions under the conditions of the experiment.

Color Changes.

Indicators.

So it appears that many phenomena find explanation in the hypothesis of Arrhenius that the ions of electrolytes exist in free condition in solutions sufficiently dilute. The changes of color on the part of indicators in the neutralization of acids and bases, and of concentrated solutions of salts upon diluting, have been taken as evidences of ionization on the part of the indicator or of the dissolved salt, but the most recent work appears to show that such an assumption is at least unnecessary.

Precipitation of Salts: Solubility Product.

The precipitation of salts from solution by the addition of a substance the molecules of which would by ionization give ions identical with one of the ions of the precipitated salt has been explained by the assumption that when the free ions which by association might constitute a precipitate reach a certain concentration which is known as the *solubility product*, precipitation takes place. But the recognized union of molecules and solvent, and consequent diminishing of the mass of solvent available for dissolving substances, must frequently be taken into consideration also.

Combination of Hydrogen and Chlorine.

Certain common phenomena, however, are difficultly reconcilable with the hypothesis of the formation of free ions by the simple act of solution. The fact that though hydrogen and chlorine combine with much evolution of heat, the product of such combination, hydrogen chloride, dissolves in much water with evolution of more heat, is not what we should expect if the act of solution involves only the breaking of hydrogen chloride, even beyond the molecular condition of hydrogen and chlorine, to hydrogen-ions and chlorine-ions.

Solution of Sodium Chloride.

So also the fact that sodium chloride dissolves in much water with absorption of less than 2 per cent. of the heat of formation of sodium chloride from the elements sodium and chlorine makes it difficult to believe that the process of solution involves simply the ionization of sodium chloride into sodium-ions and chlorine-ions. The phenomena point rather to some action of the water upon hydrogen chloride, sodium chloride, or the ions of these salts, or, in general, to some interaction between solvent and solute.

Inductive Capacity and Electrical Attractions. J. J. Thomson and Nernst have independently proposed to explain the phenomena of ionization by assuming that the solvent acts by reason of high specific inductive capacity upon molecules held together by electrical attractions of the ions, the mutual attractions of ions being diminished by the attractions between ions and induced charges in the solvent. Such a mode of ionization implies, as Fitzgerald has suggested, that the electrolyte enters into chemical reaction with the solvent, and that the assumed freedom of the ion is in reality an ever changing bondage to the solvent.

Hydrolytic Decomposition. Reychler maintains that all the phenomena of solution are better explained upon the hypothesis of hydrolytic decomposition with change of electrical charge upon molecules, the production of a charged molecule of water making of it an active unit in the phenomena of osmotic and electrical action. Such a hypothesis is quite in harmony with the thermal phenomena of neutralization and with the law of thermoneutrality, while for electrolytic phenomena a modified form of the formerly accepted hypothesis of Grotthus is applicable, according to which the system consists of an electrolyte and solvent in continuously adjustable equilibrium.

Different Views of Ionization. Whatever may be the special view which we take of the nature of *ionization*, we may use that term to indicate the formation of active units from a single molecule, and we may name the ion after an element or group of elements separated from the molecule, whether we regard it as free, or combined with the solvent, or even as a product of hydrolytic action of the solvent. For example, we may speak of the H-ion or the HO-ion, whether we follow the view of Arrhenius that the $\overset{+}{H}$ and $\overset{-}{HO}$ are free and independent individual units, or adopt the hypothesis of Nernst and Thomson of a mobile union with the solvent, or the suggestion by Reychler of hydrolytic decomposition, according to which the H-ion is really $\overset{+}{H}OH$ and the HO-ion is $H\overset{-}{O}H$. It is obvious that in the interaction of ions, however

Concentration Action. interpreted, we must take into consideration the effects of *concentration action*, as in dealing with any other individual masses of matter. The phenomena which we have to consider when we are dealing with the relations of substances in solution, even when such solutions are very dilute, may be very complex. In certain cases we are compelled to recognize the presence of undissociated molecules, polymerized molecules, combinations of molecules with the solvent, and products of reaction between solvent and solute, as well as of ions combined or uncombined with solvent. The *avidity*, or *chemical affinity*, of an acid or base is the measure of the facility with which it enters into reactions. According to any form of the ionization theory, facility of reaction should be related to freedom and mobility of the ions; and the degree of ionization in solutions of given concentration, as determined by molecular conductivity, is now generally taken as the simplest method of determining approximately the chemical affinities of acids and bases.

Avidity.

PART II

DESCRIPTIVE

PART II — DESCRIPTIVE

CHAPTER I

CLASSIFICATION AND NOMENCLATURE

In our previous study we have seen that many of the elements may be identified either as *metals*, conductors of heat and electricity, which act as positive ions in electrolysis, or as *non-metals*, which are negative ions in electrolysis. We have observed further that the metals may be arranged in a series in which the order of placing corresponds with the electrical potentials of the metals in solutions of their compounds; and that the potentials of the metals thus determined are proportionate to the powers which they possess for replacing one another from their compounds. It has also appeared that the metals as a rule exhibit basic properties and that the non-metals are for the most part acid-forming elements. When we study further the properties of the elements, other evidences of orderly relation come to light, and it becomes evident that *the elements divide themselves naturally according to physical properties and chemical behavior into groups of allied elements arranged in series.* Thus, lithium, sodium, potassium, rubidium, and cæsium constitute a group of metals which form strongly basic hydroxides and are closely allied in general properties and chemical behavior, while phosphorus, arsenic, and antimony make another group of non-metals which form acidic hydroxides and are closely similar in many relations.

Series of Allied Elements.

Triads of Döbereiner.

As early as 1817 Döbereiner noticed what appeared to him to be the natural grouping of analogous elements into threes or "triads," and pointed out a certain numerical regularity in the atomic weights of the elements which constitute the triads, the atomic weight of the central element of the triad proving to be nearly the mean of the atomic weights of two extreme elements. Thus, for

MENDELÉEFF'S PERIODIC SYSTEM

(Slightly Modified)

GROUPS	I	II	III	IV	V	VI	VII	VIII
SERIES	RH R_2O	RH_2 R_2O_2	RH_3 R_2O_3	RH_4 R_2O_4	RH_3 R_2O_5	RH_2 R_2O_6	RH R_2O_7	
1 2	1.0075 H Li 7.03	— Gl 9.1	— B 11	— C 12.00	— N 14.04	— O 16.00	— F 19	[He 4] [Ne 20]
3 4	23.05 Na K 39.15	24.36 Mg Ca 40.1	27.1 Al Sc 44.1	28.4 Si Ti 48.1	31.0 P V 51.2	32.06 S Cr 52.1	35.45 Cl Mn 55.0	[Ar 39.9] Fe 55.9 Ni 58.7 Co 59.0
5 6	63.6 Cu Rb 85.5	65.4 Zn Sr 87.6	70 Ga Yt 89.0	72.5 Ge Zr 90.6	75.0 As Cb 94	79.2 Se Mo 96.0	79.96 Br —	[Kr 81.8] Ru 101.7 Rh 103.0 Pd 106.5
7 8	107.93 Ag Cs 132.9	112.4 Cd Ba 137.4	115 In La 138.9	119.0 Sn Ce 140.25	120.2 Sb —	[127.6] Te —	126.97 I —	[Xe 128]
9 10	— —	— —	— —	— —	— Ta 183	— W 184	— —	Os 191 Ir 193.0 Pt 194.8
11 12	197.2 Au —	200.0 Hg [Ra 225]	204.1 Tl —	206.9 Pb Th 232.5	208.5 Bi —	— U 238.5	— —	

Unplaced: Pr 140.5; Nd 143.6; Sm 150; Gd 156; Tb 160; Er 166; Tm 171; Yb 173.0.

example, lithium, sodium, and potassium constitute one triad, as shown by the figures expressing the atomic weights of these elements,

$$\left.\begin{array}{ll}\text{Lithium} & = 7.03\\ \text{Sodium} & = 23.05\\ \text{Potassium} & = 39.15\end{array}\right\} \frac{7.03 + 39.15}{2} = 23.09$$

while chlorine, bromine, and iodine show similar relations in their atomic weights,

$$\left.\begin{array}{ll}\text{Chlorine} & = 35.45\\ \text{Bromine} & = 79.96\\ \text{Iodine} & = 126.97\end{array}\right\} \frac{35.45 + 126.97}{2} = 81.21$$

From this suggestion, by the gradual contributions of many thinkers, came the orderly arrangement of the elements with which the name of *Mendeléeff*, the distinguished Russian chemist, is associated, and which is known as the *Periodic System.*

Mendeléeff's System of Elements.

In Mendeléeff's system, based upon the numerical sequence of the atomic weights of the elements rather than upon exact numerical relations and differences, the element hydrogen, gaseous at ordinary temperatures, the lightest of all the elements, possessing the lowest atomic weight, 1.0075, and a valence taken always as I, naturally stands first.

The element of next atomic weight, 7.03, is lithium, possessing a valence of I, and this element is placed beneath hydrogen, and is the first member of a series showing a gradation of valence, and containing besides lithium, glucinum, with an atomic weight of 9.1, and with a valence of II; boron, with an atomic weight of 11, and a valence of III; carbon, with an atomic weight of 12, and a prevailing valence of IV; nitrogen with an atomic weight of 14.04 and a valence of III or V; oxygen with an atomic weight of 16, and an accepted valence of II; and fluorine, with an atomic weight of 19 and a prevailing valence of I. Throughout the series of elements from lithium to fluorine we note a gradation of properties from the electro-positive, metallic, base-forming lithium to the electro-negative, acid-forming non-metallic fluorine.

The next element in Mendeléeff's system, in the order of atomic weights, is sodium, electro-positive, metallic, and base-forming, of atomic weight 23.05; and though the change in atomic weight is but slight in passing from fluorine to sodium, the element sodium is very different from fluorine in its properties and relations, while it is closely analogous to lithium. For this reason sodium is placed in the system upon the line beneath lithium, and at the beginning of a new series, containing magnesium, electro-positive and basic like sodium; aluminium, less basic than magnesium; silicon, which forms a weakly acidic hydroxide; phosphorus, which is distinctly acid-forming; sulphur, still more acidic in its compounds; and chlorine, which resembles fluorine as an acidic element.

Each of these two series of elements, from lithium to fluorine, and from sodium to chlorine, consists of seven elements, in which we note a gradual transition of properties. In these series the characteristic valences of the elements follow the order I, II, III, IV, III, II, I, for their compounds with hydrogen and the halogen elements, fluorine, chlorine, bromine, and iodine, and for compounds with oxygen they follow the order I, II, III, IV, V, VI, VII. The prevailing valence relations of the elements are expressed by the typical symbols, RH, RH_2, etc., and R_2O, RO, etc., which show, respectively, the prevailing valences of the elements in the same vertical columns or groups as regards hydrogen or the halogens and as regards oxygen. On comparing the two horizontal series, it appears that the elements in the same vertical column are closely analogous in many physical properties and in chemical behavior, and that the kinds of compounds which they form are generally similar.

The remainder of the table shows similar relationships of elements, excepting that it becomes necessary to recognize a double periodicity, and to add an eighth group to contain three small series, each of which consists of three closely allied elements. Thus, in the series beginning with potassium there is no immediate repetition of the properties of the group when manganese is passed, but the elements iron, cobalt, and nickel intervene; a new series beginning with copper and ending with bromine, is completed before rubidium, an element possessed of properties closely analogous to those of potassium, is reached. It is to be noted that resemblances now develop between the group members of alternate series. Thus, potassium and rubidium are more clearly related chemically than potassium and copper.

The Periodic Law. It is plain that the Mendeléeff system shows a periodic recurrence of elements possessing similar properties. In the words of Mendeléeff, *the properties of the elements are periodic functions of their atomic weights.*

Prediction of Elements. In order, however, to make similar elements fall in the groups in which they naturally belong, when the elements are arranged according to the scheme indicated, it is frequently necessary to leave blanks in the table, especially as the atomic weights increase. In the first announcement of the periodic law a blank was found in the series between calcium, 40.1, and titanium, 48.1, and Mendeléeff predicted that for that blank an element would be found to which he gave the temporary name "eka-boron." Similarly, two blanks existed in the series between zinc, 65.4, and arsenic, 75.0. In these places were put the hypothetical elements "eka-aluminium" and "eka-silicon." To all these hypothetical elements Mendeléeff assigned properties which he had determined by observing the properties of the adjacent known elements in the group and in the series. These three elements whose discovery was thus predicted have been found — scandium, by Nilson, gallium, by Lecoq de Boisbaudran, and germanium by Winkler; and their properties have been found to correspond closely to Mendeléeff's predictions.

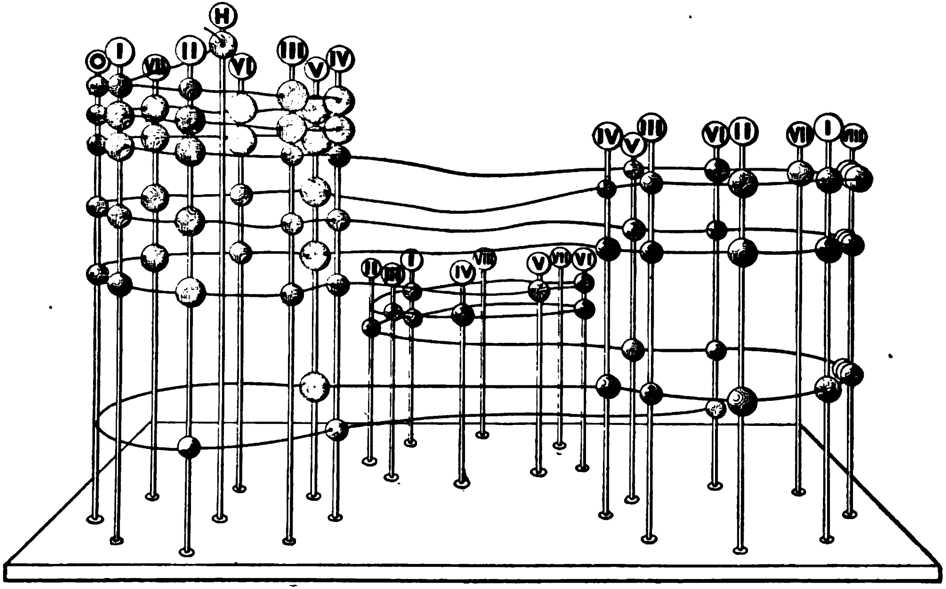
Inert Gases of the Atmosphere. At the time when the periodic system was put forward the atmospheric elements, helium, neon, argon, krypton, and xenon were not known. Distinguished by their inertness and inability so far as we are aware to form chemical compounds, there seemed at first to be no place within the periodic system for these elements; but it has been pointed out that they may not unnaturally occupy the positions of transition elements between the highly negative elements, fluorine, chlorine, bromine, and iodine, on the one hand, and lithium, sodium, potassium, rubidium, and cæsium on the other hand, where, with the exception of argon, whose atomic weight appears to be rated too high, their atomic weights would naturally place them.

Anomalies in the System. In spite of a record of great usefulness in classifying the elements and in stimulating much research, the periodic system of Mendeléeff presents many anomalies. It is noteworthy, in the first place, that argon and tellurium fall in groups to which they manifestly do not belong, if we place these elements exactly according to their atomic weights; but there are reasons for believing that the trouble with them lies in the difficulty of preparing pure materials for the atomic weight determinations. On the other hand, close relationships are suggested by the system which do not in fact exist, and some relationships which do exist are concealed in the system. Thus, in Group I we find copper, silver, and gold classed in the second division, with the quite dissimilar alkali elements, lithium, potassium, rubidium, and cæsium, making up the first division; while sodium, which belongs with the other alkali elements, is set aside in the second division of the group. Similarly, magnesium is classed more closely with zinc, cadmium, and mercury than with calcium, strontium, and barium, with which it is allied; carbon is classed with titanium rather than with silicon, which it more closely resembles; nitrogen is classified with vanadium rather than with phosphorus; manganese, a metal, is put in the same group with the strongly negative elements, fluorine, chlorine, bromine, iodine, with which it has no kinship. The elements between praseodymium, 140.5, and ytterbium, 173.0 show no clear analogies to the elements of the groups in which they would fall, if included in the table, and the reason is not apparent why iron, cobalt, and nickel should be counted as of one group, and head a group of triplet elements. For these and similar reasons chemists have not rested content with Mendeléeff's scheme of the elements, and many modifications have been proposed.

The Primary, Secondary, and Tertiary Series.

For the purposes of our work we bring forward the following arrangement of the elements as suggesting the actually existing relationships in the simplest manner with the fewest anomalies, while following the arrangement of the Mendeléeff system so far as possible, for the sake of avoiding confusion with the already familiar scheme. In this arrangement of the Periodic System, shown in the accompanying model and plan, hydrogen stands apart at the beginning of a helix and is followed by the elements, *He*, *Li*, *Gl*, *B*, *C*, *N*, *O*, *F*, in the order of their atomic weights, these elements constituting the *first period of the primary series*. The *second period of the primary series* is made up of the elements *Ne*, *Na*, *Mg*, *Al*, *Si*, *P*, *S*, *Cl*, arranged in sequence upon the second turn of the helix. The elements *Ar*, *K*, *Ca*, *Sc*, *Ti*, follow in the *third period of the primary series* upon the third turn of the helix, but at this point the period is broken and the sequence diverges to the *secondary series* represented in the model by the second helix.

The elements *V*, *Cr*, *Mn*, *Fe*, *Ni*, *Co*, *Cu*, *Zn*, *Ga*, *Ge* occupy the first turn of the second helix, and constituting a period by themselves, *the first period of the secondary series;* while the next elements in sequence, *As*, *Se*, *Br*, take up their places on the first helix to complete



PRIMARY SERIES

O	I	VII	II	VI	III	V	IV
He	Li	F	Gl	O	B	N	C
·	·	·	·	·	·	·	·
Xe	Cs	I	Ra	Te	La	Bi	Th

TERTIARY SERIES

II	III	I	IV	VIII	V	VII	VI
—	Gd	Sm	Tb	—	Pr	—	Nd
·	·	·	·	·	·	·	·
Yb	—	Tm	—	—	—	—	Er

SECONDARY SERIES

IV	V	III	VI	II	VII	I	VIII
Ge	V	Ga	Cr	Zn	Mn	Cu	Fe, Ni, Co
·	·	·	·	·	·	·	·
Pb	Ta	Tl	U	Hg	—	Au	Os, Ir, Pt

FIG. 1.—The Primary, Secondary, and Tertiary Series of Elements.

The arrangement of the elements in three series of eight groups each may be represented by a model in which large and small wooden balls, on a spiral wire, represent the common and the rare elements respectively; those balls falling in the same vertical columns representing elements in the same groups.

THE PERIODIC SYSTEM OF THE ELEMENTS

ROGEN

PRIMARY SERIES

Groups

	V	VI	VII	O	I	II	III	IV
H 1.0075				He 4	Li 7.03	Gl 9.1	B 11	C 12.00
	N 14.04	O 16.00	F 19	Ne 20	Na 23.05	Mg 24.36	Al 27.1	Si 28.4
	P 31.0	S 32.06	Cl 35.45	Ar [39.9]	K 39.15	Ca 40.1	Sc 44.1	Ti 48.1
	As 75.0	Se 79.2	Br 79.96	Kr 81.8	Rb 85.5	Sr. 87.6	Yt 89.0	Zr 90.6
	Sb 120.2	Te [127.6]	I 126.97	Xe 128	Cs 132.9	Ba 137.4	La 138.9	Ce 140.25
	Bi 208.5	—	—	—	—	Ra 225	—	Th 232.5

SECONDARY SERIES

Groups

V	VI	VII	VIII			I	II	III	IV
			a	*b*	*c*				
V 51.2	Cr 52.1	Mn 55.0	Fe 55.9	Ni 58.7	Co 59.0	Cu 63.6	Zn 65.4	Ga 70	Ge 72.5
Cb 94	Mo 96.0	—	Ru 101.7	Rh 103.0	Pd 106.5	Ag 107.93	Cd 112.4	In 115	Sn 119.0
Ta 183	W 184	—	Os 191	Ir 193.0	Pt 194.8	Au 197.2	Hg 200.0	Tl 204.1	Pb 206.9
—	U 238.5								

TERTIARY SERIES

Groups

V	VI	VII	VIII	I	II	III	IV
Pr 140.5	Nd 143.6	—	—	Sm 150.3	—	Gd 156	Tb 160
—	Er 166	—	—	Tm 171	Yb 173.0	—	—

the *third period of the primary series.* Krypton begins the sequence *Kr, Rb, Sr, Yt, Zr,* of the *fourth period of the primary series,* which is broken after zirconium to permit the interpolation of the *second period of the secondary series, Cb, Mo,* —, $\overbrace{Ru, Rh, Pd}$, *Ag, Cd, In, Sn,* in proper relation to the elements of the first period of the secondary series from *V* to *Ge.*

Then the broken *fourth period of the primary series* is continued upon the first helix with *Sb, Te, I.* Xenon begins the *fifth period of the primary series,* containing *Xe, Cs, Ba, La, Ce,* to the point where the series is broken, to introduce *the elements from praseodymium to ytterbium, constituting two incomplete periods of the tertiary series,* which, closely related among themselves, have no close relationship with other elements, and constitute a natural series apart.

The sequence then continues upon the second helix with the elements of the *third period of the secondary series, Ta, W,* —, $\overbrace{Os, Ir, Pt}$, *Au, Hg, Tl, Pb,* placed in natural relation to the elements of the second period, Cb to Sn; and then the broken fifth period of the primary series is taken up with *Bi,* —, —, —, —, *Ra,* —, *Th,* and the system ends with *U* falling, where it belongs, in the secondary series in close relation to *W.*

This arrangement makes it possible to consider by themselves in a natural way the elements of the primary series, which, as will appear, constitute by themselves a complete system in which the individual groups comprise elements of closely similar properties, while the transitions of properties, as the sequence moves from group to group, is striking and characteristic. Taking up the study of the secondary series, it will be found that the properties of the elements of this series reflect in a general way the properties of elements similarly placed in the primary series, but lateral relationships, as distinguished from group relationships, became more marked, and in the tertiary series group distinctions are largely lost. For the sake of uniformity with the Mendeléeff scheme, Group VIII has been preserved as a single group of *related triplets.* It will be noted that these elements occupy in the secondary series the position of *transition elements* between Group I of positive elements and Group VII of negative elements, just as in the primary series the inert elements of Group O occupy a similar position.

The connection between the regularities of the system of the elements and actual numerical values of the atomic weights has been the subject of much study and speculation; but at the present time, though some very interesting and suggestive approximative relations have been pointed out, it is manifest that some factor essential to the clear comprehension of the principle underlying the periodic system is lacking. Taken simply as a natural classification, the periodic system will serve us excellently as a basis upon which to rest the descriptive study of elements and compounds.

Nomenclature. In our previous work we have made use of the chemical names of substances without explanation. Before taking up the descriptive study of elements and compounds, it will be well to note briefly the system upon which these substances are named.

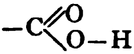
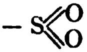
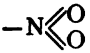
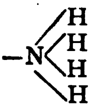
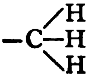
Names of Elements. *The elements are named arbitrarily.* The names of some elements have been suggested by their more characteristic physical properties. Thus, we have *chlorine,* derived from a Greek word which means "green"; *bromine,* derived from a Greek word which means "a stench"; *iodine,* derived from a Greek word which means "a violet color."

The names of some elements suggest important chemical reactions in which the elements may take part; as, for example, *hydrogen,* compounded of Greek words which mean "water-producing"; *oxygen,* compounded of Greek words which mean "acid-producing"; *nitrogen,* compounded of Greek words which mean "niter-producing."

In some cases elements have been named from the country in which they were discovered, or in which they are found; as, *columbium,* Columbia; *gallium,* Gallia; *germanium,* Germania; *scandium,* Scandinavia; *magnesium,* Magnesia.

The names assigned to the elements more recently discovered have the termination *um;* as, *cæsium,* from a Greek word meaning "sky-blue"; *lithium,* from a Greek word meaning "a stone"; *potassium,* from "potash"; *sodium,* from "soda"; *aluminium,* from a Latin word meaning "alum."

Radicals are known by special names, which generally end in the syllable yl. Thus we have:

$H-O-$	*hydroxyl*
$=C=O$	*carbonyl*
$=S=O$	*thionyl*
	*carboxyl*
	*sulphuryl*
$-C\equiv N$	*cyanogen*
	*nitroxyl*
	*ammonium*
$-P=O$	*phosphoryl*
	*methyl*

Names of Compounds. *Many compounds are named arbitrarily.* Thus we have, CH_4, *methane;* C_2H_6, *ethane;* C_3H_8, *propane;* C_6H_6, *benzene.* *The names of compounds are usually, however, derived from the names of the elements and radicals which constitute them.* Compounds of two elements or two radicals, or of one element and one radical, are called *binary compounds.* For a *binary compound* a name is made by taking the name of one component, usually the more positive, and coupling with it the name of the second component with its final syllable, or sometimes more than one syllable, changed to *ide.* Thus, we have HCl, *hydrogen chloride;* $(CH_3)Cl$, *methyl chloride;* H_2O, *hydrogen oxide;* $(C_2H_5)_2O$, *ethyl oxide;* CaO, *calcium oxide;* $(C_2H_4)O$, *ethylene oxide;* Na(OH), *sodium hydroxide;* $(C_2H_5)(OH)$, *ethyl hydroxide;* $Ca(OH)_2$, *calcium hydroxide;* $(C_2H_4)(OH)_2$, *ethylene hydroxide.*

Oxides. Compounds containing different proportions of the same elements or radicals are distinguished by indicating numerically the degrees of combination by means of suitable prefixes affixed to the second member of the name. Thus, we have N_2O, *nitrogen monoxide;* NO, *nitrogen dioxide;* N_2O_3, *nitrogen trioxide;* N_2O_4, or NO_2, *nitrogen tetroxide;* N_2O_5, *nitrogen pentoxide.*

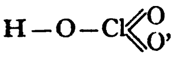
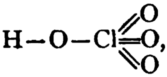
Sometimes the syllable *sub* is used to indicate a relatively small amount of one of the constituents in a compound, and the syllable *per* to indicate a relatively large amount of a constituent. Thus, Pb_2O, *lead suboxide;* PbO, *lead oxide;* PbO_2, *lead peroxide.*

Degree of presence in a compound may be indicated by making the termination of the first member of a name *ous,* to indicate a small amount of the corresponding constituent, and by suffixing the syllable *ic* to indicate a high amount of that constituent. For example: Cu_2O, *cuprous oxide;* Cu_2Cl_2, *cuprous chloride;* CuO, *cupric oxide;* $CuCl_2$, *cupric chloride.*

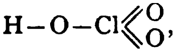
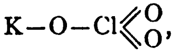
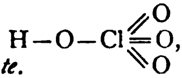
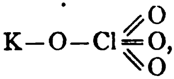
Oxides from which hydroxides having the properties of acids are formed are sometimes termed *anhydrides,* taking their distinguishing names from the acids which they form with water and of which they are the anhydrides, i.e. *derived by removal of water.* For example: SO_2, *sulphurous anhydride;* SO_3, *sulphuric anhydride.*

Compounds formed by substituting an element or radical in a given molecule by some other element or radical are often named by combining the names of the substituting elements or radicals with those of the original substances. We have CH_4, *methane;* CH_3Cl, *monochlormethane;* CH_2Cl_2, *dichlormethane;* $CHCl_3$, *trichlormethane;* CCl_4, *tetrachlormethane.*

Hydroxides. *Hydroxides,* compounds which contain the radical hydroxyl, $-O-H$, generally take their name from the oxide from which they may be considered to be derived. For example, we have the bases: KOH, *potassium hydroxide;* $Ca(OH)_2$, *calcium hydroxide;* $Fe(OH)_3$, *ferric hydroxide.*

Several *acidic hydroxides* of the same characteristic element may be distinguished by special names to denote the degree of valence of the element. As in the case of the oxides, the terminations *ous* and *ic* are used to indicate the lower and higher valences respectively; and sometimes the prefixes *hypo* and *per* are used as well. For example: $H-O-Cl$, *hypochlorous acid;* $H-O-Cl=O$, *chlorous acid;*  $\mathrm{H-O-Cl}\begin{smallmatrix} /\!\!/\mathrm{O} \\ \backslash\!\!\backslash\mathrm{O}\end{smallmatrix}$, *chloric acid;*  $\mathrm{H-O-Cl}\begin{smallmatrix} /\!\!/\mathrm{O} \\ =\mathrm{O} \\ \backslash\!\!\backslash\mathrm{O}\end{smallmatrix}$, *perchloric acid.*

Some *oxyhydroxides,* derived from two or more molecules of normal hydroxides, bear names indicating the number of molecules from which they are derived. Thus we have *disulphuric acid,* $H_2S_2O_7$, derived from two molecules of normal sulphuric acid, H_2SO_4, and *tetracupric hydroxide,* $Cu_4O_3(OH)_2$, derived from four molecules of normal cupric hydroxide, $Cu(OH)_2$. Such compounds, however, sometimes bear special names, such as *metaphosphoric acid,* HPO_3, and *pyrophosphoric acid,* $H_4P_2O_7$, derived from normal phosphoric acid, H_3PO_4.

Salts. The name of a *neutral salt* is made from the name of the characteristic element of the base to which the salt is related, coupled with a name derived from the name of the acid from which the salt is derived. When the name of the acid ends in *ic,* the second part of the name of the derived salt ends in *ate;* when the name of the acid ends in *ous,* the second part of the name of the salt ends in *ite.* We have: $H-O-Cl$, *hypochlorous acid;* $K-O-Cl$, *potassium hypochlorite;* $H-O-Cl=O$, *chlorous acid;* $K-O-Cl=O$, *potassium chlorite;*  $\mathrm{H-O-Cl}\begin{smallmatrix} /\!\!/\mathrm{O} \\ \backslash\!\!\backslash\mathrm{O}\end{smallmatrix}$, *chloric acid;*  $\mathrm{K-O-Cl}\begin{smallmatrix} /\!\!/\mathrm{O} \\ \backslash\!\!\backslash\mathrm{O}\end{smallmatrix}$, *potassium chlorate;*  $\mathrm{H-O-Cl}\begin{smallmatrix} /\!\!/\mathrm{O} \\ =\mathrm{O} \\ \backslash\!\!\backslash\mathrm{O}\end{smallmatrix}$, *perchloric acid;*  $\mathrm{K-O-Cl}\begin{smallmatrix} /\!\!/\mathrm{O} \\ =\mathrm{O} \\ \backslash\!\!\backslash\mathrm{O}\end{smallmatrix}$, *potassium perchlorate.*

Acidic salts and *basic salts* have names similar to those of neutral salts, except that the individual hydrogen-ions or the hydroxyl-ions left in the molecule are indicated. We have: $KHSO_4$, *potassium hydrogen sulphate;* KH_2PO_4, *potassium dihydrogen phosphate;* K_2HPO_4, *dipotassium hydrogen phosphate;* $BiOH(NO_3)_2$, *bismuth monohydroxynitrate;* $Bi(OH)_2NO_3$, *bismuth dihydroxynitrate.*

Oxysalts are named from the oxyacids to which they are related. Thus we have *sodium disulphate,* $Na_2S_2O_7$, corresponding to disulphuric acid, $H_2S_2O_7$.

With this preliminary explanation, other relations of nomenclature will be readily understood as the occasion requires.

CHAPTER II

PRIMARY SERIES—HYDROGEN

Hydrogen, H, 1.008[1]

WITH hydrogen, the lightest of all the elements and possessed of the lowest atomic weight, we begin our systematic study of the elements and their compounds.

Hydrogen. Hydrogen, observed by Paracelsus in the sixteenth century, and recognized in 1766 by Cavendish, who called it "inflammable air," occurs in free condition in our world only in small amount. It is found in traces in our atmosphere, and more abundantly in some volcanic vapors, in oil wells, and among the products of putrefaction of organic matters. It is a colorless, odorless, tasteless gas. It is the lightest known substance, a cubic centimeter of it weighing 0.0000899 grm., less than $\frac{1}{14}$ as much as the weight of an equal volume of air. It is sometimes taken as a convenient standard of specific gravity for gases. The weight of an atom of hydrogen taken as 1 is sometimes used as a standard of atomic weights, but it is more convenient to arrange atomic weights with reference to the atomic weight of oxygen taken as 16, when the atomic weight of hydrogen is 1.0075. The specific gravity and molecular weight of hydrogen in terms of oxygen/32 is 2.015.

Preparation of Hydrogen. *Hydrogen may be obtained in quantity by decomposing by appropriate means water or other suitable compounds of hydrogen.*

Decomposition of Water by Heat. *Hydrogen may be prepared from water by the dissociating action of heat.* When molten platinum is poured into water, bubbles of gas arise which consist of hydrogen and oxygen. The great heat of the molten platinum raises the temperature of the immediately adjacent water to a point at which it is dissociated, while the cooling effect of the mass of water upon the mixed gases is such as to prevent their combination, which takes place only at or above a certain temperature of ignition.

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[1] More accurately 1.0075.

$$\begin{matrix}\mathrm{H-O-H}\\ \mathrm{H-O-H}\end{matrix} = \mathrm{H-H} + \mathrm{O{=}O}$$

The experiment may be arranged in such manner that the uncombined gases produced by dissociation of the water may be partially separated by reason of their different capacities for passing through a porous earthenware wall, the lighter hydrogen passing through the wall more rapidly than the heavier oxygen. Thus, when water vapor is passed through a porous clay tube surrounded by a jacket of non-porous porcelain, and the tube and jacket are heated to white heat in a furnace, a temperature may be attained sufficient to partially dissociate the water vapor. The lighter hydrogen passes more easily through the porous tube into the outer jacket, from which the gas largely hydrogen may be collected by a delivery tube, while the gas largely oxygen may be similarly collected directly from the inner tube.

Action of Elements upon Water. *Some of the more electro-positive elements decompose water and liberate hydrogen spontaneously at ordinary temperature.* We have only to throw a small bit of potassium on a surface of water to have a violent effervescence of hydrogen accompanied by the liberation of sufficient heat to set on fire the hydrogen evolved in contact with the floating potassium. When much water is present, potassium hydroxide, KOH, is formed, which remains dissolved in the excess of water, and may be recovered by evaporation of the water by heating.

$$\begin{matrix}\mathrm{H-O-H}\\ \mathrm{H-O-H}\end{matrix} + \begin{matrix}\mathrm{K}\\ \mathrm{K}\end{matrix} = \begin{matrix}\mathrm{K-O-H}\\ \mathrm{K-O-H}\end{matrix} + \mathrm{H-H}$$

When little water is present and the temperature is high enough, or when the potassium hydroxide formed in the presence of an abundance of water is heated with more potassium, potassium oxide, K_2O, and hydrogen are the products.

$$\mathrm{H-O-H} + \begin{matrix}\mathrm{K}\\ \mathrm{K}\end{matrix} = \left.\begin{matrix}\mathrm{K}\\ \mathrm{K}\end{matrix}\right\rangle\mathrm{O} + \mathrm{H-H}$$

Sodium acts similarly upon water, producing sodium oxide when the water is deficient and the temperature high,

$$\mathrm{H-O-H} + \begin{matrix}\mathrm{Na}\\ \mathrm{Na}\end{matrix} = \left.\begin{matrix}\mathrm{Na}\\ \mathrm{Na}\end{matrix}\right\rangle\mathrm{O} + \mathrm{H-H}$$

or sodium hydroxide, $NaOH$, in presence of a sufficient amount of water.

$$\begin{array}{c}H-O-H\\H-O-H\end{array}+\begin{array}{c}Na\\Na\end{array}=\begin{array}{c}Na-O-H\\Na-O-H\end{array}+H-H$$

In these reactions less heat is evolved than in the corresponding reaction of potassium under similar conditions, so that the hydrogen evolved about the floating sodium does not ordinarily inflame as it meets the air unless the sodium be held still in one place so that the heat of the reaction may not be dissipated rapidly. The hydrogen evolved in the action may be easily collected by simply slipping the sodium, pressed into a section of glass tubing, beneath the end of an inverted test-tube filled with and standing in water.

Other elements act like potassium and sodium upon water, but the temperature necessary to start and sustain the action is higher. A quantity of powdered magnesium contained in a test-tube of cold water shows no evidence of decomposing the water. When we heat the water to boiling, however, an effervescence of hydrogen begins. Magnesium, less electro-positive than potassium, must be heated before it sets up the decomposition of water.

$$\begin{array}{c}H-O-H\\H-O-H\end{array}+Mg=Mg\begin{array}{l}\diagup O-H\\\diagdown O-H\end{array}+H-H$$

Iron may also be employed to liberate hydrogen from water. For this purpose bits of scrap-iron or nails are placed in a strong iron tube, and gradually heated to redness in a furnace, a current of steam being slowly driven through the tube. The temperature of this reaction is above that at which iron hydroxide is decomposed. It is the oxide of the element which is formed in this case. The residue is the "blacksmith's scale," or "magnetic oxide of iron."

$$Fe_3 + 4\,H_2O = Fe_3O_4 + 4\,H_2$$

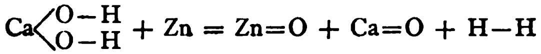
Carbon, though electro-negative and very unlike potassium and other metals, will nevertheless decompose water, taking the oxygen from it. When carbon in the form of coal or coke is heated to incandescence in the presence of steam, a mixture is produced which consists principally of hydrogen, and carbon monoxide or carbon dioxide according to the temperature and conditions.

$$H-O-H + C = C=O + H-H$$

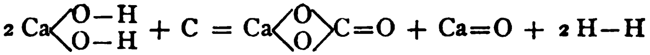
$$\begin{array}{c}H-O-H\\H-O-H\end{array}+C=C\begin{array}{l}\diagup\!\!\diagup O\\\diagdown\!\!\diagdown O\end{array}+\begin{array}{c}H-H\\H-H\end{array}$$

Water Gas. The mixture of hydrogen and carbon monoxide, purified, if necessary, from carbon dioxide, is the so-called "water gas," used commonly for heating purposes and as a constituent of an illuminating gas.

Action of Elements upon Hydroxides. *Hydrogen may be liberated from certain hydroxides by the action of certain elements which become oxidized.* Thus, both zinc and carbon are oxidized when heated with calcium hydroxide, $Ca(OH)_2$, hydrogen being evolved.



$$Ca\begin{matrix}\diagup O-H\\ \diagdown O-H\end{matrix} + Zn = Zn{=}O + Ca{=}O + H-H$$



$$2\,Ca\begin{matrix}\diagup O-H\\ \diagdown O-H\end{matrix} + C = Ca\begin{matrix}\diagup O \diagdown\\ \diagdown O \diagup\end{matrix}C{=}O + Ca{=}O + 2\,H-H$$

Electrolysis of Hydroxides. *Hydrogen may be liberated from certain acidic hydroxides and from other acids by the action of the electric current.* When a dilute water solution of sulphuric acid, H_2SO_4, is submitted to the action of a suitable electric current, the positively charged hydrogen-ions are gathered at the negative pole, where they yield their charges and pass into the form of hydrogen gas; while the HSO_4 ions, or the SO_4 ions, pass to the positive pole and there, giving up their charges, break up, and form free oxygen and sulphur trioxide which combines with water to form again sulphuric acid.

$$(a)\ H_2SO_4 = \overset{+}{H} + \overset{-}{HSO_4}$$

$$(b)\ 4\,\overset{+}{H} + 4\,\overset{-}{HSO_4} + 2\,H_2O = \overbrace{2\,H_2}^{-\text{pole}} + \overbrace{4\,H_2SO_4 + O_2}^{+\text{pole}}$$

or,

$$(a)\ H_2SO_4 = 2\,\overset{+}{H} + \overset{-}{SO_4}$$

$$(b)\ 4\,\overset{+}{H} + 2\,\overset{-}{SO_4} + 2\,H_2O = \overbrace{2\,H_2}^{-\text{pole}} + \overbrace{2\,H_2SO_4 + O_2}^{+\text{pole}}$$

In like manner hydrochloric acid is decomposed by the electric current into hydrogen and chlorine.

$$(a)\ HCl = \overset{+}{H} + \overset{-}{Cl}$$

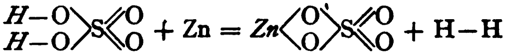
$$(b)\ 2\,\overset{+}{H} + 2\,\overset{-}{Cl} = \overbrace{H_2}^{-\text{pole}} + \overbrace{Cl_2}^{+\text{pole}}$$

Hydrogen may be liberated in the electrolysis of certain basic hydroxides, by the action upon water of the metal set free by the electric current. When a dilute water solution of potassium hydroxide is submitted to the action of a suitable electric current, electrolysis takes place with the evolution of hydrogen and oxygen. The first action of the current is to gather the ions at the poles, the positive potassium-ion at the negative pole and the negative hydroxyl-ion at the positive pole. Upon giving up their positive electrical charges the potassium-ions react with the water to form potassium hydroxide and liberate hydrogen, while the hydroxyl-ions, upon yielding up their negative charges, form oxygen and water.

$$(1)\ KOH = \overset{+}{K} + \overset{-}{\overbrace{OH}}$$

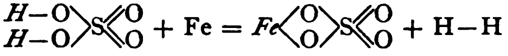
$$(2)\ 4\overset{+}{K} + \overbrace{4\,OH}^{-} + 4\,H_2O = \overbrace{4\,KOH + 2\,H_2}^{-\text{pole}} + \overbrace{2\,H_2O + O_2}^{+\text{pole}}$$

Action of Elements upon Acids. *The action of certain elements upon acids results in the formation of salts in which the elements employed are positive ions, while hydrogen is liberated.* The action of zinc upon sulphuric acid in dilute water solution is an example of this, the zinc replacing the hydrogen in the acid and forming zinc sulphate, $ZnSO_4$, which remains in solution.

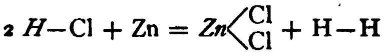


This reaction furnishes a convenient method for the preparation of hydrogen for laboratory purposes. The zinc is best employed in granulated form. If the acid solution is not sufficiently dilute, the action may be retarded by the deposition of solid zinc sulphate upon the zinc.

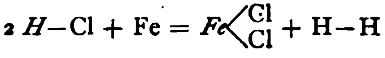
Iron acts similarly but less rapidly upon dilute sulphuric acid, with formation of iron sulphate, $FeSO_4$, in solution, though for commercial purposes this reaction is preferred to that of zinc and sulphuric acid.



Zinc acts similarly upon hydrochloric acid, HCl, with evolution of hydrogen and formation of zinc chloride, $ZnCl_2$, in solution.



Iron acts upon hydrochloric acid similarly to liberate hydrogen and form iron chloride, $FeCl_2$, in solution.



In like manner we find that magnesium and tin and some other metals will liberate hydrogen, not only from appropriately chosen acids like sulphuric acid and hydrochloric acid, but also from acetic acid, $H(C_2H_3O_2)$, and other acids similar to acetic acid. In general, *hydrogen is usually evolved when a metal acts upon an acid in dilute solution.* It should be noticed, however, that hydrogen is not usually evolved by the action of a metal upon nitric acid, or upon other acids capable, as is nitric acid, of oxidizing the hydrogen as it is liberated.

Action of Elements upon Basic Hydroxides. *In certain cases the hydrogen of a basic hydroxide may be replaced by a suitable element with the formation of a salt in which the replacing element enters the negative ion.* Potassium hydroxide, KOH, when boiled with zinc, is slowly acted upon, and potassium zincate, K_2ZnO_2, a peculiar unstable salt, is formed in solution, while hydrogen is evolved.

$$\begin{matrix} K-O-H \\ K-O-H \end{matrix} + Zn = \begin{matrix} K-O \\ K-O \end{matrix}\!\!>\!Zn + H-H$$

Physical Properties. Hydrogen, though ordinarily gaseous, may be liquefied, and even solidified, by pressure at a sufficiently low temperature. The process is attended with experimental difficulties which have only been overcome in comparatively recent time, because the critical temperature of hydrogen is in the neighborhood of — 220°. Such an extreme temperature is difficult to reach, but even this degree of cold and more may now be produced. If the pressure upon a gas or liquid, capable of vaporizing rapidly under reduction of pressure, be suddenly lowered, the consequent expansion will produce in the gas or liquid a lower temperature. Carbon dioxide, for example, may be liquefied by compressing it and cooling it in ice and salt; and the cooled liquid thus obtained, when permitted to evaporate by relieving the pressure, absorbs a great deal of heat, so much in fact, that a part of the liquid carbon dioxide becomes exceedingly cold and freezes. So liquefied carbon dioxide may be used to produce intense cold for refrigerating purposes. Hydrogen may in this way be cooled to a very low temperature, but not, however, sufficiently low to liquefy it. If now the sufficiently cooled gas be allowed to expand, a portion of it in expanding absorbs a great deal of heat, and in a properly constructed apparatus arranged for successive compressions, coolings, and expansions, the expansion of a part of the hydrogen will cool the remainder of the gas to a temperature very close to that at which the gas becomes a liquid. In this manner Dewar, following the procedure of Wroblewski, and allowing hydrogen, cooled to –205° and under a pressure of 180 atmospheres, to enter a vacuum at 200°, succeeded in producing liquid hydrogen with a boiling point of –240° under atmospheric pressure. More recently Dewar has succeeded, at a temperature of –255°, only 18° removed from the absolute zero, in reducing hydrogen to the condition of a white crystalline solid.

Chemical Properties. The chemical relations of hydrogen are most varied and important. It combines with many elements, toward most of which it is electro-positive, and it acts as a positive ion in acids. It can hardly be classed among the metals, since in liquid form it is a non-conductor of electricity, though it forms its most stable and definite binary compounds with non-metallic elements, like oxygen, nitrogen, carbon, and chlorine. Hydrogen burns in oxygen or air, forming water. Ignited at the mouth of a jet, it burns quietly, but when a mixture of hydrogen with air or oxygen is raised to the point of ignition, about 200°, it explodes violently. Though non-luminous, the flame is very hot; and it is this evolution of heat which keeps the hydrogen burning at the jet in air, and which spreads the chemical action throughout a mixture of hydrogen and oxygen, effecting the sudden production of a mass of water vapor, the expansion of which constitutes the explosion. Hydrogen also combines with most electro-positive elements, like potassium and sodium.

Occlusion. Hydrogen is absorbed or "occluded" by spongy platinum in marked degree, and the hydrogen thus condensed combines with oxygen at ordinary temperature, as may be shown in *Döbereiner's lamp*, in which a jet of hydrogen is spontaneously ignited when allowed to impinge upon a bit of freshly ignited platinum sponge exposed to air. Hydrogen is occluded by palladium at 100° to an amount six hundred times the volume of the latter, and to still greater extent when palladium is made the negative electrode at which hydrogen is evolved in an electrolytic cell. These compounds of hydrogen with the metals seem to be of the nature of the ordinary *alloys*, or mixtures of metals. Since, moreover, like ordinary solutions, they exist as mixtures in many proportions, they may be regarded as *solid solutions* rather than definite single chemical compounds. The hydrogen in process of liberation from such compounds, however, possesses extraordinary chemical activity, and in this respect is comparable to the hydrogen in *nascent condition*, at the instant of its liberation by electrolysis or chemical action.

Spectra. Hydrogen, like all other substances, emits light when heated to a sufficiently high temperature. White light, as we all know, when passed through a prism, is deviated from a straight course and spread out into a continuous band of rainbow colors. When sent through a fine slit, and then through a prism, the white light is resolved and spread out in a *spectrum* upon a plane surface, placed to receive it, as a continuous band made up of a succession of images of the slit in all colors ranging from red to violet. If the slit is illuminated by a ray of a single color, the image of the slit will appear on the plane surface in the form of a single line. The continuous band of color is called a *continuous spectrum* and a spectrum consisting of one or more lines is a *line spectrum.*

While solids and liquids, when sufficiently hot, emit white light which is resolved by the prism into a continuous spectrum, gases and vapors emit simpler colors which, when passed through the slit and prism, appear as line spectra. Such line spectra, moreover, are characteristic of the substances which emit them. The study of such spectra constitutes the *spectrum analyses* first practiced by Bunsen and Kirchoff; and the instrument employed, which is merely an apparatus by which an illuminated slit is observed in such manner that the position of any given line in the spectrum may be noted, is the *spectroscope*, a simple form of which is shown in the figure.

The Spectroscope. The adjustable slit on the end of the tube *A* is illuminated by the light to be investigated. The rays passing the slit are gathered by a lens and sent in a parallel ray through the prism *P* and are gathered again by the object glass of the observing telescope so that the eye placed at *E* will see the spectrum produced by images of the slit, single lines if the spectrum is a line spectrum, and a continuous band of images of the slit if the spectrum is continuous. Placed opposite the second face of the prism is a little telescope carrying a scale, the reflection of which in the face of the prism is seen, a little above the spectrum, by the eye at *E*. By means of

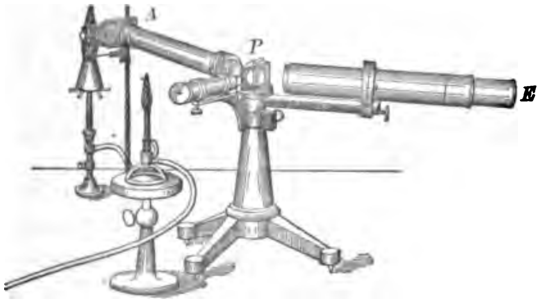


FIG. 2. — The Spectroscope.

this arrangement it is possible to determine the position of any given line in the spectrum produced by the particular instrument in use. To observe the line spectrum of a substance it is only necessary to illumine the slit of the instrument by the incandescent gas or vapor of the substance.

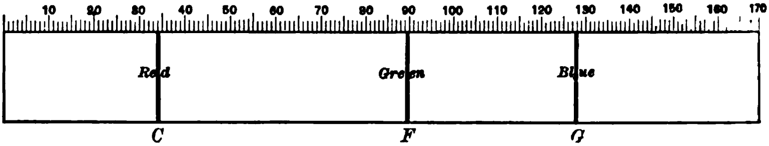


FIG. 3.—Line Spectrum of Hydrogen. (Adapted from Roscoe.)

Many solids and liquids may be vaporized by the heat of a Bunsen burner, for some solids it is necessary to use the electric arc, while the spectra of gases are obtained by passing the sparks of an induction coil between electrodes in tubes, known as Geissler's tubes, containing the gases under very low pressure. Hydrogen, submitted to the action of an induction spark, gives a red light, which, when analyzed by the spectroscope, is shown to consist of a red line accompanied by a green line and a blue line. These lines have always the same relative position in the spectrum produced by a given spectroscope. They are characteristic of hydrogen.

If while observing a line spectrum a powerful white light is placed behind the luminous gas or vapor, the continuous spectrum of the white light will form a background for the line spectrum, against which, if the white light is sufficiently powerful, the lines will look dark. The spectrum of hydrogen for example, when viewed against the brilliant continuous spectrum of an electric arc light, will appear as three dark lines occupying the position of the lines of hydrogen which, when seen by themselves, are red, green, and blue. This phenomenon is the *reversal* of the spectrum, the immense importance of which becomes apparent when we study the light coming to us from the sun. The *solar spectrum* consists of a brilliant continuous spectrum crossed by many dark lines, the positions of which in the spectrum coincide with the bright lines of many known

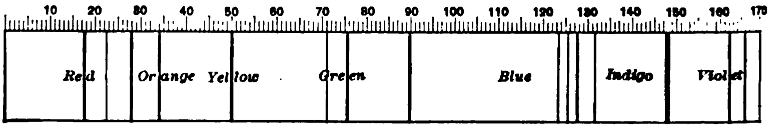


FIG. 4.—Continuous Spectrum of Sunlight, with Fraunhofer Lines. (Adapted from Roscoe.)

substances examined by themselves with the same instrument. Among the dark lines, the *Fraunhofer lines* as they are called, of the solar spectrum, we find the lines which correspond to the positions of the hydrogen lines when observed directly against a non-luminous background. So it appears that the white of the *photosphere* or luminous envelope of the sun comes to us through masses of incandescent hydrogen in its upper atmosphere. This is a phenomenon which is easily observed with the simplest sort of spectroscope. The astronomers who work with telescopes which can be so directed as to take in only the light from the outer edge of the sun are able to observe with the spectroscope attached to the telescope the bright red, green, and blue lines of hydrogen. So we know that free hydrogen, which exists in our world in only small amounts, is present in immense masses in our sun, and in the other blazing suns which we know as fixed stars, and in the celestial nebulæ.

Fraunhofer Lines.

Summary.

We note, in summary, that hydrogen may be obtained from hydroxides — from water by the dissociating action of heat, and by the action of elements, positive and negative, — from acids and bases by electrolysis, and by the action of metals or non-metals. Hydrogen may be liquefied and solidified. Hydrogen is very active chemically, combining with other elements directly and entering into many compounds. In acids it is the positive ion and in basic hydroxides it is a part of the negative hydroxyl-ion. Hydrogen is occluded in large quantities by certain metals. Hydrogen emits a characteristic complex spark spectrum consisting of one red line, one green line, and one blue line.

CHAPTER III

PRIMARY SERIES — GROUP O

THE INERT GASES OF THE ATMOSPHERE

HELIUM, He, 4
NEON, Ne, 20
ARGON, Ar, [39.9]
KRYPTON, Kr, 81.8
XENON, Xe, 128

Group O: Inert Gases. IT has been pointed out that the elements of Group O in the primary series stand next to hydrogen and in an intermediate position between the strongly electro-negative acid-forming elements of the series and the strongly electro-positive base-forming elements of the same series. These elements mark the point of transition from the properties of one extreme to those of the other opposite extreme, and offer, after hydrogen, a convenient starting point for the consecutive study by groups of the elements of the primary series. The elements of Group O of the primary series are all colorless gases, and all exist in free condition, hydrogen and helium in the atmosphere of the sun, and helium, neon, argon, krypton, and xenon in the atmosphere of our world, although in exceedingly small quantities.

Like hydrogen in that they exist ordinarily in gaseous form, and give when incandescent characteristic line spectra, the elements helium, neon, argon, krypton, xenon, constitute a group of elements otherwise peculiar. No one of these elements is known to combine with any other element; they are all chemically inactive. To identify these elements we have to rely upon their physical properties, chief of which for the purpose are the spectral lines of the incandescent gases.

Helium. Though it seems most remarkable that we should go to the sun to make the first discovery of an element existing upon our own earth, it is a fact that the existence of the first element of the series was noted in the sun by Lockyer in 1867, who attributed the dark line D_3 of the solar spectrum to an element not then known upon the earth. As this element was peculiar to the sun, it was named ***helium***, from the Greek word for sun. In 1892 Palmieri found the bright spectral line of helium in volcanic material thrown out by Vesuvius, and in 1895

Ramsay evolved from the mineral *uraninite* a gas which when incandescent gave the D_3 line of helium, as well as four other lines which had not been previously attributed to helium. So helium, abundant in the sun, does exist, though very sparingly, upon the earth, and is a constituent, though a very minute one, of our atmosphere, as Kayser was the first to show. It has recently been observed that helium is present in the emanations from certain *radio-active* substances. When an induction spark is passed between platinum electrodes through helium, the gas is absorbed by the platinum, but is again evolved upon heating the platinum. The behavior of helium is like that of hydrogen toward platinum and palladium, and the solid solution of helium in platinum is the only known association of helium with another element which suggests in any way that helium may be possessed of chemical activity. Under normal conditions helium has a specific gravity of 3.96; it can be liquefied by means of vaporizing liquid hydrogen.

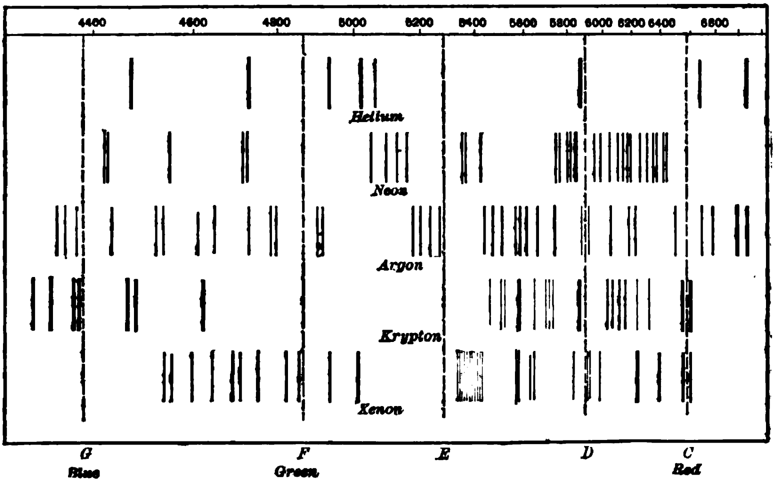


FIG. 5.—Line Spectra of Inert Gases of the Atmosphere. Scale, 10^{-10} meter wave-length. (Adapted from Travers.)

The Residual Gas. When air is freed from oxygen and the minor constituents, principally water vapor and carbon dioxide, there is left a "residual gas" which consists principally of nitrogen. Until recently it was supposed that this gas contained nothing but nitrogen, although Cavendish, in 1783, noted that while the greater part of this "atmospheric nitrogen," when mixed with oxygen, could be oxidized by the aid of an induction spark to products absorbed by potassium hydroxide, a portion always remained unchanged under this treatment.

Lord Rayleigh, in 1892, observed that purified air, when freed from oxygen by being first "sparked" and then passed over hot copper, left a gas which has a specific gravity greater than that of pure nitrogen prepared from ammonia or nitric acid. Lord Rayleigh and Ramsay investigated this new gas, which is present to the extent of 0.935 per cent. of the air by volume, so that one person inhales about 20 liters of it daily. By liquefying it, using vaporizing liquid air as a cooler, and subjecting it to fractional distillation, the substance has been separated into a trace of *helium*, *argon*, which constitutes the larger part of it, and the allied elements *neon*, *krypton*, *xenon*, which have different specific gravities, and give characteristic spectral lines when incandescent. The last four gases are heavier than helium, neon having a specific gravity of 19.94, argon of 39.92, krypton of 81.76, and xenon of 128, and a similar gradation is seen in other physical properties of these gases. Thus, while the boiling points of helium and neon are unknown, the boiling point of argon is −186.1°, that of krypton, −151.67°, and that of xenon −109.10°. All these substances, helium, neon, argon, krypton, xenon, apparently chemical elements, are alike in being chemically inactive.

Argon.

Neon, Krypton, Xenon.

Specific Heats.

There is another point in which these inert gases are alike and peculiar. The specific heat of a gas has a fixed value, if the gas, when heated, is kept at constant or unchanging volume, not being allowed to expand. The specific heat has other values, however, when the gas is allowed to expand, because in expanding the gas is doing work; but if the pressure upon the gas is kept constant while it is allowed to expand, another fixed value of the specific heat is obtained. For any given gas the ratio of the specific heat under constant pressure, Cp, to the specific heat under constant volume, Cv, has a fixed value. In accordance with the principles of thermodynamics it can be shown that the value of this ratio, $\frac{Cp}{Cv}$, depends upon the amount of internal work done within the individual molecule; and where no work is done at all within the individual molecule the ratio should have the value 1.66. In monatomic gases, in which the molecule consists of one atom, and in which, therefore, no work is expended in the motion of minor constituent parts of the molecules, the ratio should be 1.66. Fortunately the ratio $\frac{Cp}{Cv}$ is easily found by determining the wave-length of a given sound vibration in the given gas at definite temperature and pressure. In this manner we find the ratio $\frac{Cp}{Cv}$ to be 1.66 for mercury, which is known to be monatomic, because its atomic weight and molecular weight, the specific gravity to oxygen/32, are the same; while the corresponding ratio for diatomic gases like hydrogen and oxygen is approximately 1.41. The ratios of the specific heats under constant pressure to the specific heats under constant volume of helium, neon, argon, krypton, and xenon are found, like that of mercury, to have the value 1.66, which shows either that the molecules of these gases are monatomic, or else that the atoms constituting a molecule are held together so firmly as to be incapable of independent motion at the ordinary temperatures. The simpler hypothesis with which to explain the ratio of the specific heats of the inert gases is the assumption that their molecules are monatomic. The atomic weights of helium, neon, argon, krypton, and xenon are, therefore, expressed by the same numbers which stand for their molecular weights, and for their specific gravities, in terms of the ideal gas, oxygen/32.

Summary. *The inert elements of the atmosphere are all colorless gases, liquefiable by extremely high pressure and low temperature, but without chemical activity. From considerations involving the specific heats we hold these gases to be monatomic, their specific gravities being identical with both their atomic and molecular weights. These elements are recognized by their characteristic spectra.*

CHAPTER IV

PRIMARY SERIES—GROUP I

LITHIUM, Li, 7.03
Sodium, Na, 23.05
Potassium, K, 39.15
RUBIDIUM, Rb, 85.5
CÆSIUM, Cs, 132.9

Group I: Alkali Elements. THE elements of Group I of the primary series, lithium, sodium, potassium, rubidium, and cæsium, are strikingly similar to one another, and are known as the *alkali elements*. They are never found free, and only in recent years have they been prepared in pure condition. Sodium and potassium were first prepared from their compounds by Sir Humphry Davy in 1807. They are soft, lustrous metals of low specific gravity, oxidizing when exposed to dry air, readily combustible, decomposing water spontaneously, with formation of hydroxides which are the strongest bases known. Taken as a whole, the elements exhibit a fairly uniform gradation of properties. The alkali elements appear in compounds as positive ions, and ordinarily exhibit a valence of I.

The simple alkali compounds are generally soluble in water, white in color, dissociated by high heat, and thus yielding, even in the Bunsen flame, colors and spectra characteristic of the metals. It was by the observation of their spectra that rubidium and cæsium were discovered by Bunsen and Kirchhoff in 1860.

Rocks. The compounds of the alkali elements occur very widely distributed in *rocks*, and in the products formed by the disintegration of rocks, sodium and potassium in great abundance, lithium sparingly, and rubidium and cæsium in very small amounts. Those rocks of the earth's crust which were formed by the cooling and solidification of material from a state of fusion or solution at high temperature

Weathering.

consist of ***minerals*** which are elements, or compounds, or mixtures of elements or compounds, of definite physical properties, and usually crystalline. In these older rocks are many minerals which contain compounds of the alkali elements. In ***granite***, for example, we find ***feldspars***, such as ***orthoclase***, $KAlSi_3O_8$, or ***albite***, $NaAlSi_3O_8$, associated with some form of ***mica***, such as ***muscovite***, $H_2KAl_3Si_3O_{12}$. These are typical of many other rock-forming compounds of potassium and sodium, containing ***silica***, SiO_2 (silicon dioxide), and other oxides, known generally as ***silicates***. By the disintegration or ***weathering*** of such rocks, under the action of atmospheric agencies,—the freezing of water in crevices, the chemical action of carbon dioxide and water,—begins the formation of the ***soil;*** and the products of the decay

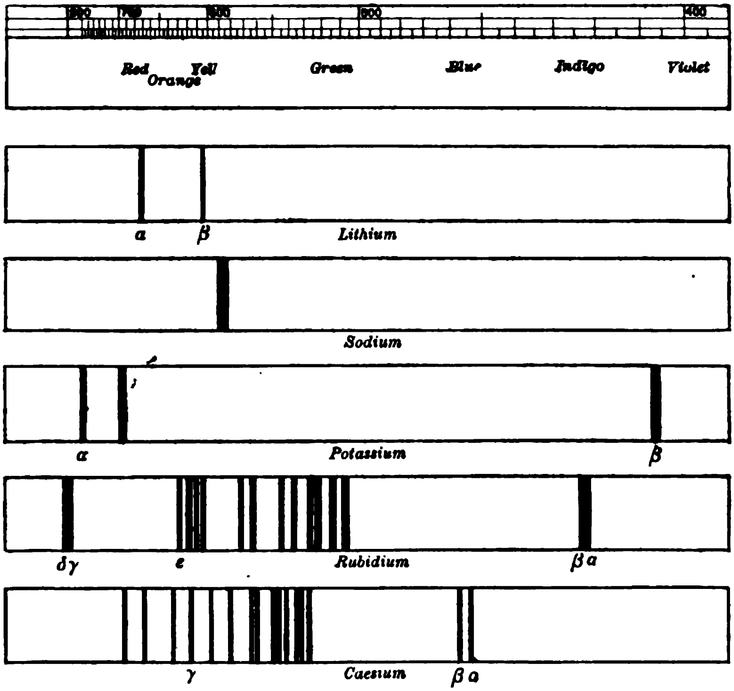


FIG. 6.—Line Spectra of Vapors of the Alkali Compounds. Scale, 10^{-9} meter wave-length. (Adapted from Roscoe.)

of plant life, once started in the soil, tend to further the disintegration and decomposition of the material of the rocks.

Sea Water. Soluble compounds of the alkali elements may be washed from the soil by the rains, to appear in springs or to be carried in rivers to the sea. The distillation of pure water from the surface of the sea and the return of the water to the sea charged with soluble compounds from the soil result naturally in the concentration of these soluble materials in the sea water. The ocean now contains about 3.5 per cent. of its weight of dissolved mineral matter, of which four fifths is sodium chloride and a small proportion potassium chloride, together with minute amounts of lithium chloride and traces of the chlorides of rubidium and cæsium. When the sea water is allowed to evaporate completely, these salts, with some others, chiefly magnesium chloride, magnesium sulphate, and calcium sulphate, are obtained in the solid residue. In various parts of the earth we find concentrated *brines*, and sometimes solid residues, produced by the evaporation of former seas of salt water.

The Stassfurt Deposit. At Stassfurt, in Germany, for example, there is a natural deposit of salts nearly 3000 feet thick, which consists for the most part of a mass of *halite* or *rock salt* (sodium chloride), NaCl, in thin layers, separated by layers of *anhydrite* (calcium sulphate), $CaSO_4$, above which lie strata containing potassium and magnesium minerals, deposited in the last stage of evaporation of the waters. The most important of these strata, lying nearest the surface, has the composition shown in the table:

MINERAL	SYMBOL	PER CENT.
Carnallite	$KCl . MgCl_2 . 6 H_2O$	55–60
Kainite	$K_2SO_4 . MgSO_4 . MgCl_2 . 6 H_2O$	Variable
Sylvite	KCl	Variable
Halite (rock salt)	$NaCl$	20–25
Kieserite	$MgSO_4 . H_2O$	16

Deposits of rock salt, generally without the overlying potassium salts, also occur in various other parts of the world. In our own country such deposits lie beneath the surface in parts of New York and Michigan.

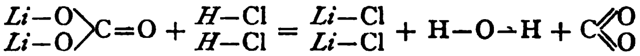
Land Plants and Sea Plants. When soluble sodium salts are released from the rocks in the formation of soil, they are easily washed out and begin their journey in solution to the sea. The potassium salts, on the other hand, are likely to be entrapped on the way. Potassium salts are seized upon by plants feeding upon the soil, while the sodium salts for the most part escape. When plants cease to live, and decay, the potassium compounds are returned again to the soil, to be taken up by other plants or to be washed away. The living plants upon the land serve, therefore, as a repository of potassium salts, to promote the growth of succeeding generations of plants. Sometimes, however, it becomes necessary to increase the content of potassium in poor soils by the addition of potassium salts as fertilizers. When land plants are burned, the potassium salts taken from the soil are changed for the most part into potassium carbonate, which may be dissolved, or *lixiviated*, out of the ashes, and obtained in solid form by evaporating the solution. It is this property of holding potassium compounds, possessed by land plants, which keeps the potassium salts from accumulating in the sea in corresponding measure with the sodium salts, and thereby makes it possible to use the ashes of land plants as a source from which to obtain potassium compounds. On the other hand, the sea plants possess the characteristic property of taking up sodium compounds from the sea water, and so the ashes of sea plants may serve as a source of sodium carbonate, just as the ashes of land plants may be lixiviated to obtain potassium carbonate.

From the sea waters and brines containing the extracts from soils and disintegrated rocks, as well as from residues of the natural evaporation of soil waters, the compounds of sodium and potassium may be obtained; and the ashes of land plants and sea plants also constitute available starting points for the preparation of these salts. Compounds of lithium, rubidium, and cæsium are prepared more advantageously from certain rare minerals.

LITHIUM, Li, 7.03

Compounds of lithium occur widely but generally sparingly distributed in rocks, soils, and mineral waters. Certain minerals contain this element in considerable amounts, such as the silicates, *lepidolite* and *spodumene*, and the complex phosphates, *triphylite*, *lithiophylite*, and *amblygonite*. Certain mineral waters likewise carry soluble lithium salts in appreciable quantities, and the presence of lithium is recognized in the ash of certain plants such as tobacco and the beet. Advantage is taken of the greater insolubility of lithium carbonate to precipitate this salt from the mixture of soluble alkali salts obtained from mineral springs, or from lithium minerals by suitable treatment.

From lithium carbonate, purified by dissolving in water charged with carbon dioxide and reprecipitating by removing the carbon dioxide, salts of lithium may be prepared by the action of appropriate acids. By the action of hydrochloric acid upon lithium carbonate, Li_2CO_3, soluble *lithium chloride*, LiCl, may be obtained,



$$\begin{matrix}Li-\mathrm{O}\\Li-\mathrm{O}\end{matrix}\!\!>\mathrm{C}=\mathrm{O}+\begin{matrix}H-\mathrm{Cl}\\H-\mathrm{Cl}\end{matrix}=\begin{matrix}Li-\mathrm{Cl}\\Li-\mathrm{Cl}\end{matrix}+\mathrm{H}-\mathrm{O}-\mathrm{H}+\mathrm{C}\begin{matrix}\nearrow\mathrm{O}\\\searrow\mathrm{O}\end{matrix}$$

and from lithium chloride, lithium may be obtained by electrolysis of the fused salt or of the salt dissolved in pyridine,

$$2\,Li-\mathrm{Cl} = 2\,Li + \mathrm{Cl}-\mathrm{Cl}$$

Lithium is a silvery white metal, of specific gravity 0.59, melting at 180°, and capable of decomposing water at the ordinary temperature with evolution of hydrogen and formation of lithium hydroxide,

$$2\,\mathrm{Li} + 2\,\mathrm{H-O-H} = 2\,\mathrm{Li-O-H} + \mathrm{H-H}$$

from which many characteristic salts of lithium may be prepared, in which lithium is a univalent positive ion.

Lithium oxide, Li_2O, white and crystalline, obtained by ignition of lithium nitrate in contact with copper, shows a tendency when heated in oxygen to take on more oxygen, with partial formation of yellowish *lithium dioxide*, Li_2O_2.

Lithium hydroxide, LiOH, white and soluble in water, is most easily made by acting upon lithium sulphate, $LiSO_4$, with barium hydroxide, $Ba(OH)_2$, insoluble barium sulphate, $BaSO_4$, and soluble lithium hydroxide being formed.

Lithium chloride, LiCl, white and deliquescent, may be crystallized at ordinary temperatures from its water solution; below 10°, however, the salt takes on water of crystallization, forming $LiCl \cdot 2H_2O$.

Lithium carbonate, Li_2CO_3, white and soluble in about one hundred parts of water, is precipitated from concentrated solutions of lithium chloride, LiCl, by the action of a soluble carbonate. Lithium carbonate dissolves to the extent of four per cent. in water charged with carbon dioxide, probably forming lithium hydrogen carbonate, and is again precipitated upon removal of the excess of carbon dioxide. Advantage may be taken of this behavior to purify lithium carbonate.

Lithium phosphate, $2Li_3PO_4 \cdot H_2O$, white, crystalline, and difficultly soluble, is precipitated from solutions of lithium salts by sodium phosphate, Na_2HPO_4, and ammonium hydroxide, NH_4OH. The metal lithium, ignited in nitrogen, forms *lithium nitride*, Li_3N, and in hydrogen forms *lithium hydride*, LiH.

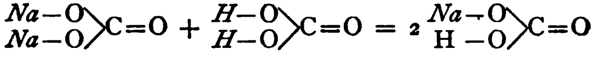
Lithium salts give to the Bunsen flame a crimson color, and exhibit a characteristic spectrum consisting of a crimson-red line, with a very faint orange-red line.

Sodium, Na, 23.05

Soda. From the ashes of sea plants the sodium carbonate of commerce was formerly made. At the present time salt water beach plants are still cultivated in Spain and Southern France to make crude sodium carbonate, or *soda*, as the extract of the ashes was formerly called. While this form of the soda industry is now of local importance only, the sodium carbonate obtained by the historic process of lixiviating the ashes of sea plants and evaporating the solution will serve us best as a starting point in our study of typical compounds of sodium. We shall consider later the modern commercial methods for the manufacture of sodium carbonate.

Sodium Carbonate. *Sodium carbonate*, Na_2CO_3, is found native, notably in California. It may be lixiviated from the ashes of sea plants, and is produced conveniently from sodium chloride by the processes of Leblanc and of Solvay, which will be considered later. It dissolves easily in water, from which it may be crystallized in prismatic crystals, having the symbol $Na_2CO_3 \cdot 10H_2O$. This is common "washing soda." At 100° the crystals become anhydrous and disintegrate.

When carbon dioxide, CO_2, in solution, in effect the unstable carbonic acid, H_2CO_3, acts upon the neutral crystallized sodium carbonate, Na_2CO_3, the acidic *sodium hydrogen carbonate*, $NaHCO_3$, is formed.

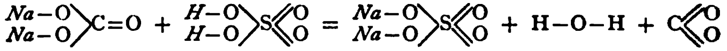


$$\left.\begin{matrix}Na-O\\Na-O\end{matrix}\right>C=O + \left.\begin{matrix}H-O\\H-O\end{matrix}\right>C=O = 2\left.\begin{matrix}Na-O\\H-O\end{matrix}\right>C=O$$

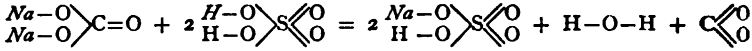
The same reaction takes place when carbon dioxide is passed into a saturated solution of neutral sodium carbonate, inasmuch as the acidic carbonate is much less soluble than the neutral carbonate. The sodium hydrogen carbonate is "baking soda." When heated moderately, it gives off carbon dioxide, readily forming the neutral salt, and this process goes on even in the boiling solution of the salt.

Sodium Carbonate and Acids. *Both sodium carbonate and sodium hydrogen carbonate are decomposed by nearly all acids with the liberation of carbon dioxide, and the formation of corresponding sodium salts in which sodium is the positive ion.*

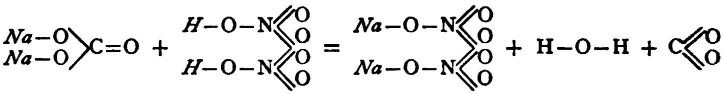
By acting upon sodium carbonate, Na_2CO_3, with sulphuric acid, carbon dioxide, CO_2, is set free, and the resulting solution contains *sodium sulphate*, Na_2SO_4.



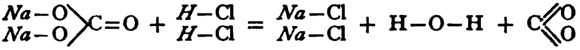
By changing the proportions of the reacting substances, *sodium hydrogen sulphate*, $NaHSO_4$, may be obtained.



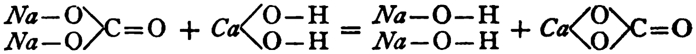
If nitric acid is used to decompose sodium carbonate, *sodium nitrate*, $NaNO_3$, is formed in solution.



Similarly, if hydrochloric acid is used, *sodium chloride*, NaCl, is the product.

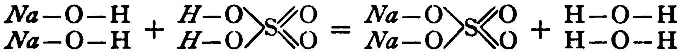


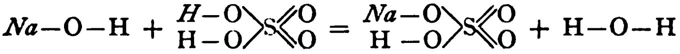
Sodium Hydroxide. When the sparingly soluble calcium hydroxide, $Ca(OH)_2$, is added to a solution of the soluble sodium carbonate, Na_2CO_3, and the mixture boiled, a metathesis takes place, the insoluble calcium carbonate, $CaCO_3$, being precipitated, while *sodium hydroxide*, NaOH, remains in solution. The action takes place slowly, because the calcium hydroxide needed to complete the action goes into solution very gradually.



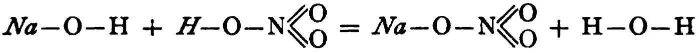
After settling out the insoluble calcium carbonate and evaporating the solution, a white residue of sodium hydroxide remains. This is "caustic soda." The crude product is sometimes dissolved in alcohol to purify it, and the residue, still containing some water after evaporation of the alcohol, is cast into sticks.

Sodium Hydroxide and Acids. *Sodium hydroxide may be used to neutralize acids, and thus produce salts in which sodium is the positive ion.* With sulphuric acid, sodium hydroxide, NaOH, gives *sodium sulphate*, Na_2SO_4, or *sodium hydrogen sulphate*, $NaHSO_4$, according to the proportions of the reagents.





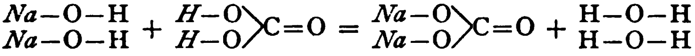
With nitric acid, sodium hydroxide gives *sodium nitrate*, $NaNO_3$.

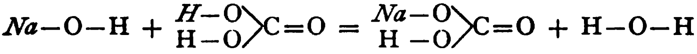


With hydrochloric acid, sodium hydroxide gives *sodium chloride*, NaCl.

$$Na-O-H + H-Cl = Na-Cl + H-O-H$$

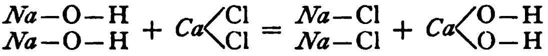
With carbon dioxide, CO_2 dissolved in water (in effect carbonic acid, H_2CO_3), sodium hydroxide gives *sodium carbonate*, Na_2CO_3, or *sodium hydrogen carbonate*, $NaHCO_3$.





Sodium Hydroxide and Salts.

Sodium hydroxide interacts with the salts of many elements to form hydroxides. When sodium hydroxide, NaOH, is added to a solution of calcium chloride, $CaCl_2$, the sparingly soluble calcium hydroxide, $Ca(OH)_2$, may be precipitated, and sodium chloride remains in solution.



Salts of other elements and radicals are readily acted upon by sodium hydroxide with the formation of sodium salts and hydroxides. Ammonium salts are thus decomposed, and inasmuch as the ammonium hydroxide formed is unstable, ammonia and water are among the final products. Thus, when we act upon ammonium chloride, NH_4Cl, with sodium hydroxide, NaOH, we get sodium chloride, NaCl, and ammonium hydroxide, NH_4OH, or ammonia, NH_3, and water.

$$NaOH + NH_4Cl = NaCl + NH_4OH, \text{ or}$$

$$NaOH + NH_4Cl = NaCl + NH_3 + H_2O$$

St is now used as a short term for $[C_{18}H_{35}O_2]$ St
(1812) stands for Stearic acid.

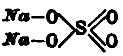
Soaps. The reaction of sodium hydroxide with salts to form other hydroxides is largely employed in ***soap making***. Ordinary soap is usually a sodium salt of a complex carbon acid of the group known as *fatty acids*. Animal and vegetable *fats* consist chiefly of salts of these fatty acids and glycerine, a weakly basic hydroxide. Thus stearin, $C_3H_5(C_{18}H_{35}O_2)_3$, contained in tallow, is a salt of *glycerine*, $C_3H_5(OH)_3$, and *stearic acid*, $H(C_{18}H_{35}O_2)$. When we boil a mixture of stearine and sodium hydroxide, a metathesis takes place by which the sodium of the sodium hydroxide changes place with the positive radical of the stearin, forming glycerine, and leaving a residue of ***sodium stearate***, $Na(C_{18}H_{35}O_2)$. This is ordinary hard soap.

$$3\,NaOH + C_3H_5\overset{St_3}{(C_{18}H_{35}O_2)_3} = 3\,Na\overset{St}{(C_{18}H_{35}O_2)} + \overset{glycerine.}{C_3H_5(OH)_3}$$

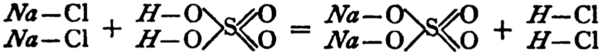
The action of a basic hydroxide upon the glycerine salt of a fatty acid to form glycerine and a soap or salt of the fatty acid is called *saponification*, and the use of this term is sometimes extended to cover the similar action of a basic hydroxide upon other compounds of carbon. In practice the animal fats and many kinds of vegetable oils are employed in soap making. When the soap is dissolved in water, it is partially hydrolyzed, giving a small proportion of free alkali hydroxide to which the detergent effect is largely due.

Wood Pulp. Sodium hydroxide has recently found a similar application in the preparation of *wood pulp*, useful in the manufacture of paper. Soft woods, such as poplar, cottonwood, and basswood, are most suitable for the purpose, since they consist of nearly pure *cellulose*, $(C_{12}H_{20}O_{10})_m$, containing small amounts of resinous material. When the chipped or ground wood is digested for some hours with a solution of sodium hydroxide, the resinous material is saponified, forming soaps soluble in water, and these dissolve in the liquid, and may be washed away with the excess of sodium hydroxide, leaving the cellulose fiber as a soft pulp.

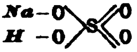
Sodium Salts. We have considered how sodium sulphate, sodium nitrate, and sodium chloride may be produced by the action of acids upon sodium carbonate or sodium hydroxide. These salts are white solids soluble in water, and are commercial products of great importance.



Sodium sulphate, Na_2SO_4, made by the action of sulphuric acid upon sodium carbonate or sodium hydroxide, occurs in solution in many waters and brines, and in large deposits both in the anhydrous condition, and in the crystallized form, $Na_2SO_4 \cdot 10H_2O$, known as *Glauber's salt*. It is produced in large quantities in the first stage of the Leblanc soda manufacture by heating sodium chloride (salt) and sulphuric acid together, hydrogen chloride gas being expelled in the process.

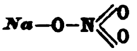


There are other commercial processes by which it is produced from common salt, to be used in the manufacture of sodium carbonate and of glass.



Sodium hydrogen sulphate, $NaHSO_4$, formed by the action of sulphuric acid upon sodium sulphate, is a white crystalline solid, soluble in water.

$$Na_2SO_4 + H_2SO_4 = 2\ NaHSO_4$$



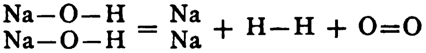
Sodium nitrate, $NaNO_3$, which may be produced by the action of nitric acid upon sodium carbonate or sodium hydroxide, occurs naturally as "Chili saltpeter," in a deposit many square miles in extent, lying in the desert region on the western coast of South America. The natural rock, or *caliche*, containing the salt is boiled with water, and the crude material is obtained by crystallization, to be shipped to Europe and America for use in the manufacture of potassium nitrate and nitric acid, and as a fertilizer. The salt crystallizes in white rhombohedra very similar to cubes, and so it is called "cubic saltpeter." It is hygroscopic, taking in moisture easily from the atmosphere.

Na–Cl

Sodium chloride, NaCl (salt), made in pure condition by the action of hydrochloric acid upon sodium carbonate or sodium hydroxide, occurs as the mineral *halite* (rock salt) in many countries, and often in such a condition of purity that it need only be mined and crushed to be ready for use. Mention has already been made of the chief European deposit at Stassfurt. In the United States large salt deposits lie beneath the surface in New York and Michigan, from which the salt is extracted by sinking shafts and running water into them, which, when it is saturated, is pumped out and evaporated to crystallize the comparatively pure salt. The water of *salt springs*, and *brines*, also yield sodium chloride by evaporation, and in warm countries the sea water is evaporated by the sun's rays, and finally by artificial heat, to get the impure salt. Some salt is produced in California in this manner. In Russia, the first concentration of sea water is made by freezing out the pure water, thus leaving a strong brine to be evaporated.

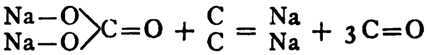
Sodium chloride crystallizes ordinarily from water in transparent anhydrous cubes which arrange themselves in curious hopper-like formations, though at − 10° it crystallizes in tables having the composition $NaCl \cdot 2\,H_2O$. It is about equally soluble in hot water and in cold water. It is used in making a *freezing mixture* with ice. Sodium chloride is necessary as a food, furnishing the chlorine of the hydrogen chloride which is a constituent of the gastric juice of the stomach. The greater part of the sodium chloride of commerce is used in the manufacture of sodium compounds, principally sodium carbonate, and of hydrochloric acid.

Sodium. *Sodium* was first produced by Sir Humphry Davy, in 1807, by the electrolysis of fused sodium hydroxide.



$$\begin{matrix}Na-O-H\\Na-O-H\end{matrix} = \begin{matrix}Na\\Na\end{matrix} + H-H + O=O$$

It was formerly prepared commercially by igniting a mixture of sodium carbonate and coal in an iron retort, condensing the vapor of the volatile metal in iron receivers, and collecting the metal under rock oil.



$$\left.\begin{matrix}Na-O\\Na-O\end{matrix}\right\rangle C=O + \begin{matrix}C\\C\end{matrix} = \begin{matrix}Na\\Na\end{matrix} + 3\,C=O$$

More recently sodium hydroxide has been reduced commercially by treatment with a combination of carbon with finely divided iron.

Sodium is a soft, lustrous, white metal of specific gravity 0.9348 at 0°, melting at 95.6°, boiling at 742°, oxidizing on exposure to air, and decomposing water at ordinary temperatures.

Sodium Oxides. At temperatures below 300° sodium combines with oxygen to form *sodium dioxide*, Na_2O_2 (sodium peroxide). The dioxide loses oxygen when strongly heated, and tends to form *sodium monoxide*, Na_2O, which, however, is not known certainly in pure condition. Sodium dioxide is, however, acted upon by water, with evolution of oxygen, and the formation of sodium hydroxide, which is also formed when water is decomposed by sodium.

Spectrum. The sodium compounds are slightly volatile at high temperatures. They give to the Bunsen flame an intense yellow color, and exhibit a characteristic spectrum consisting of two closely adjacent yellow lines.

Summary. *In summarizing the reactions of sodium and its compounds, we note that sodium carbonate is acted upon by acids with the formation of corresponding sodium salts, which are generally white, soluble in water, and not readily decomposed by heating. By acting upon sodium carbonate with calcium hydroxide, the strongly basic soluble sodium hydroxide is formed, which will neutralize acids with the formation of sodium salts. By the electrolysis of fused sodium hydroxide, sodium is obtained, which oxidizes to sodium dioxide, and which decomposes water spontaneously to form sodium hydroxide. The compounds of sodium impart a yellow color to flame, and exhibit a characteristic spectrum of two closely adjacent yellow lines.*

Manufacture of Sodium Carbonate. *The commercial manufacture of sodium carbonate from sodium chloride (salt) utilizes several of the reactions with which we became familiar in our study of the sodium compounds.* The older process of Leblanc is still retained in long-established plants, but is destined, no doubt, to replacement finally by the more economical Solvay process.

Leblanc Process. The *Leblanc Soda Process,* invented by Nicolas Le Blanc, in 1775, in competition for a prize offered by the French Academy, depends primarily upon three chemical reactions. When sodium chloride, NaCl, is acted upon by sulphuric acid, gaseous hydrogen chloride is evolved, and sodium sulphate, Na_2SO_4, remains behind.

$$(1)\ 2\,NaCl + H_2SO_4 = Na_2SO_4 + 2\,HCl$$

The sodium sulphate may be reduced to sodium sulphide, Na_2S, by heating it with carbon, carbon dioxide being evolved.

$$(2)\ Na_2SO_4 + 2\,C = Na_2S + 2\,CO_2$$

When sodium sulphide and calcium carbonate (limestone) are heated in intimate mixture, sodium carbonate is formed.

$$(3)\ Na_2S + CaCO_3 = Na_2CO_3 + CaS$$

The first part of the process is commenced in a covered iron pan, and is completed in some form of *reverberatory furnace,* so arranged that while the fuel is kept separate from the charge to be heated, the flames come directly in contact with it. The gaseous hydrogen chloride is led away to a tower and absorbed in water to be utilized as a by-product. The fused mass from the furnace, known as *salt cake,* contains 95 per cent. of sodium sulphate. It is crushed, mixed with finely broken limestone and powdered coal, and fused in a reverberatory furnace until carbon monoxide, CO, appears as a sign of the end of the process. The carbon monoxide comes from the reaction between carbon and an excess of limestone.

$$CaCO_3 + C = CaO + 2\,CO$$

The crude mixture thus obtained, containing 45 per cent. of sodium carbonate and a large quantity of calcium sulphide, is called *black ash*. This is lixiviated with water. The resulting *tank liquor* contains 24 per cent. of sodium carbonate, including some sodium hydroxide which can be converted into sodium carbonate by the action of carbon dioxide. By evaporating the tank liquor crude *soda ash* is obtained, from which pure sodium carbonate may be made by solution and crystallization. The residue of *tank waste*, containing calcium sulphide, lime, coal, and ashes, is utilized in various ways. In Europe the Leblanc process has been employed for a century and a quarter, and, at the present time, its product equals that of the Solvay process.

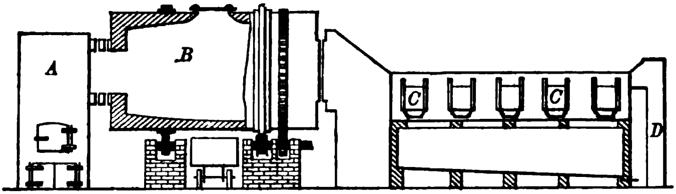


FIG. 7.—Revolving Black Ash Furnace used in the Manufacture of Sodium Carbonate by the Leblanc Process. *A*, Firebox. *B*, Rotating Cylinder. *CC*, Evaporating Pan. *D*, Chimney. (Thorp.)

Solvay Process. The *Solvay Soda Process*, devised in 1863 by Ernest Solvay, a Belgian, depends upon the fact that sodium hydrogen carbonate is but slightly soluble in a cold ammonia solution of common salt. It involves three simple reactions. When carbon dioxide, CO_2, is passed into a water solution of ammonia. NH_3, ammonium hydrogen carbonate, NH_4HCO_3, is formed.

$$(1)\quad NH_3 + H_2O + CO_2 = NH_4HCO_3$$

Ammonium hydrogen carbonate reacts with sodium chloride, NaCl, to form sodium hydrogen carbonate, $NaHCO_3$, and ammonium chloride.

$$(2)\quad NaCl + NH_4HCO_3 = NaHCO_3 + NH_4Cl$$

When sodium hydrogen carbonate is heated, carbon dioxide and water are evolved, and sodium carbonate is formed.

$$(3)\quad 2\,NaHCO_3 = Na_2CO_3 + H_2O + CO_2$$

In the actual practice carbon dioxide under pressure is passed into a concentrated solution of salt, saturated with ammonia, at a temperature which does not exceed 40°, and the sodium hydrogen carbonate thus precipitated is separated from the solution, dried, and ignited.

$$NaCl + NH_4OH + CO_2 = NaHCO_3 + NH_4Cl$$

The sodium chloride used as raw material is obtained by boring into the salt deposits, flooding the wells with water, and pumping to the surface and evaporating the resulting brines. Part of the ammonia required is obtained by treating with lime the ammonium compounds contained in "gas liquor," and part is formed by acting upon the by-product ammonium chloride with slaked lime residues. Part of the carbon dioxide required is produced by heating limestone in a *kiln* of special form, a residue of quicklime being also formed from which slaked lime is obtained, and part of the carbon dioxide is produced by heating the sodium hydrogen carbonate formed as an intermediate product.

The brine is placed in a tank provided with a perforated bottom, under which is introduced ammonia gas, which rises through the liquid until the latter is saturated, the mixture being kept cool by cold water circulating in coils. The saturated ammoniacal solution is passed through a *settling tank* and thence into a *carbonating tower*, which consists of segments, each of which has a large opening in the bottom, covered by a perforated dome, and each of which is cooled by a system of pipes carrying cold water. The ammoniacal brine is forced under pressure through a pipe entering at a point a little above the middle of the tower, and the

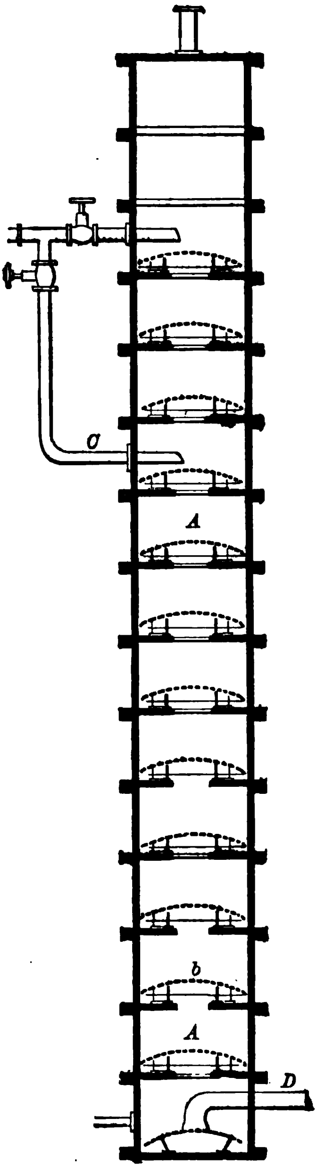


FIG. 8.—Carbonating Tower used in the Manufacture of Sodium Carbonate by the Solvay Process. (Lunge.) *AA*, Segments. *b*, Perforated Dome. *C*, Pipe admitting Brine charged with Ammonia. *D*, Pipe for admitting cooled Carbon Dioxide.

carbon dioxide, cooled and purified, and also under pressure, is forced into the tower at the base, and rises in bubbles through the perforation of the domes in each segment of the tower, thus coming in close contact with the cooled ammoniacal brine. The sodium hydrogen carbonate formed is held in suspension in a thick milky solution, which is drawn off from the base of the tower, and filtered or passed through a centrifugal machine to separate the sodium hydrogen carbonate from the ammonium chloride and the excess of sodium chloride held in solution. The sodium hydrogen carbonate recovered is washed with water, and calcined in large covered cast-iron pans or ovens, being thus converted into soda ash, or sodium carbonate. The gases from the carbonating tower and the calcining ovens are cooled and purified, and the carbon dioxide obtained from them is used in the carbonating tower. The mother liquors from which the sodium hydrogen carbonate has been crystallized, and the wash waters, are treated with slaked lime to recover the ammonia, which is utilized in the first stage of the process.

Manufacture of Sodium Hydroxide. Sodium hydroxide is manufactured either by acting upon sodium carbonate, Na_2CO_3, with calcium hydroxide, $Ca(OH)_2$, as previously described, or by electrolyzing a solution of sodium chloride, NaCl, as will be described in our consideration of the element chlorine.

Potassium, K, 39.15

Potash. Just as sea plants, taking sodium from the sea, may serve as a source of sodium salts, so the land plants may be utilized for the production of potassium salts. By lixiviating the ashes of land plants, a solution is obtained which contains a large amount of potassium compounds, chiefly potassium carbonate. The crude solution or *lye* is evaporated, and the resulting impure *potash* by recrystallization gives the white commercial *pearlash*. This process is largely carried on in Russia, Sweden, and America, the wood of the elm, maple, and birch being used. The refuse from the manufacture of sugar from the sugar beet is also utilized for the same purpose. By further treating the pearlash, pure potassium carbonate may be produced.

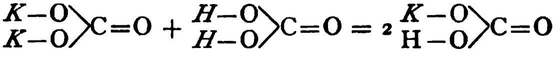
Potassium Carbonate. Potassium carbonate is also made from the potassium chloride, KCl, of the immense deposits of Stassfurt, by a process, similar to the Leblanc soda process, in which the potassium chloride is treated with sulphuric acid, and the resulting potassium sulphate, K_2SO_4, is heated with limestone and charcoal, pure potassium carbonate being obtained from the residue.

(1) $2\,KCl + H_2SO_4 = K_2SO_4 + 2\,HCl$

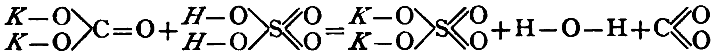
(2) $K_2SO_4 + 2\,C + CaCO_3 = K_2CO_3 + CaS + 2\,CO_2$

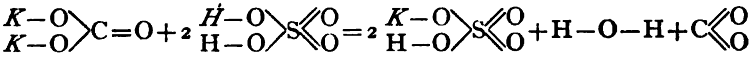
Other methods, which need not be considered here, are also employed in making potassium carbonate and other potassium salts from the native potassium chloride.

Potassium carbonate, K_2CO_3, is ordinarily an anhydrous white powder, but crystals of the composition $2\,K_2CO_3 \cdot 3\,H_2O$, may be obtained by evaporation of the concentrated solution. It is used in making Bohemian glass. By carbon dioxide and water (in effect carbonic acid, H_2CO_3), it is changed into the crystalline *potassium hydrogen carbonate*, $KHCO_3$, which is less soluble than the neutral carbonate.

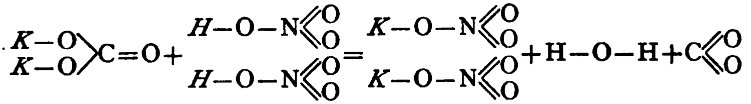


Potassium Carbonate and Acids. *Potassium carbonate is attacked by acids with evolution of carbon dioxide and formation of soluble potassium salts in which potassium is the positive ion.* Sulphuric acid forms with potassium carbonate, K_2CO_3, *potassium sulphate*, K_2SO_4, or *potassium hydrogen sulphate*, $KHSO_4$, according to the proportions acting.

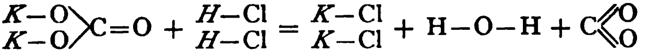




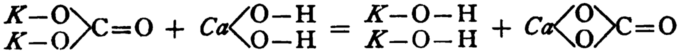
Nitric acid forms *potassium nitrate*, KNO_3.



Hydrochloric acid forms *potassium chloride*, KCl.



Potassium Hydroxide. When potassium carbonate, K_2CO_3, is treated with the calcium hydroxide, $Ca(OH)_2$ insoluble calcium carbonate, $CaCO_3$, is precipitated and *potassium hydroxide*, KOH, remains in solution.



From this solution, decanted from the precipitated calcium carbonate and concentrated, best in a silver dish if in small quantities, a residue may be obtained, which, poured into molds, cools to form solid sticks.

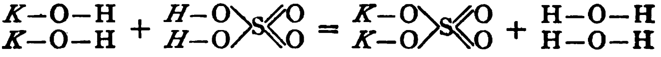
Potassium hydroxide is also formed in solution when potassium is thrown on water, hydrogen being evolved in the process.

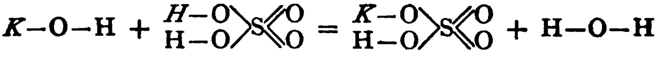
In the electrolytic decomposition of potassium chloride, in which chlorine appears as a negative ion, and potassium as a positive ion, the liberated potassium acts upon the water to form potassium hydroxide as a final product of the electrolysis.

Potassium hydroxide, KOH, is a white, brittle solid. It is deliquescent, readily absorbing water from the air. If left exposed to air containing carbon dioxide, it soon changes into potassium carbonate. It dissolves in water with great readiness, evolving heat in the process and forming a thick liquid which has a corrosive action upon the skin and other organic matter. It is the strongest of the common bases. It is used sometimes in making soft soap, but it is important chiefly as a chemical reagent for neutralizing acids, absorbing carbon dioxide, and for forming other hydroxides.

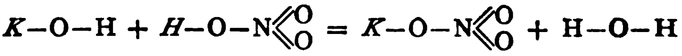
Potassium Hydroxide and Acids.

By the action of acids upon potassium hydroxide, salts are formed in which potassium is the positive ion. When sulphuric acid acts upon potassium hydroxide, KOH, either *potassium sulphate*, K_2SO_4, or *potassium hydrogen sulphate*, $KHSO_4$, is formed.





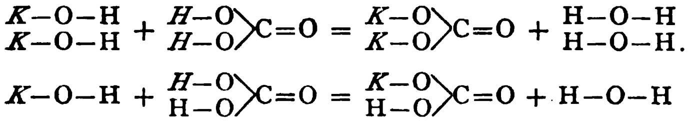
Nitric acid, when allowed to act upon potassium hydroxide, will form *potassium nitrate*, KNO_3.



And hydrochloric acid in like manner will form *potassium chloride*, KCl.

$$K\text{—O—H} + H\text{—Cl} = K\text{—Cl} + \text{H—O—H}$$

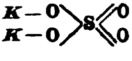
When carbon dioxide, CO_2, dissolved in water (in effect carbonic acid, H_2CO_3), acts upon potassium hydroxide, KOH, *potassium* *carbonate*, K_2CO_3, or *potassium hydrogen carbonate*, $KHCO_3$, are formed.



Soaps. By boiling potassium hydroxide, KOH, with *animal fats* or *vegetable oils*, potassium soaps, the so-called "soft soaps," are formed. The *stearin* in tallow, $C_3H_5(C_{18}H_{35}O_2)_3$, thus yields glycerine, $C_3H_5(OH)_3$, and potassium stearate, $K(C_{18}H_{35}O_2)$, a soft soap.

$$3\,KOH + C_3H_5(C_{18}H_{35}O_2)_3 = 3\,K(C_{18}H_{35}O_2) + C_3H_5(OH)_3$$

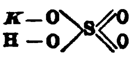
Potassium Salts. The common salts of potassium, which as we have seen may be made by acting upon potassium carbonate or potassium hydroxide with acids, are generally white solids, soluble in water, and are commercial products of importance.



Potassium sulphate, K_2SO_4, produced by the action of sulphuric acid in regulated amounts upon potassium carbonate or potassium hydroxide, is also formed when sulphuric acid acts in proper amounts upon potassium chloride.

$$2\,KCl + H_2SO_4 = K_2SO_4 + 2\,HCl$$

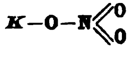
It crystallizes from water, in which it is moderately soluble, in anhydrous prisms.



Potassium hydrogen sulphate, $KHSO_4$, is formed when potassium sulphate is acted upon by sulphuric acid.

$$K_2SO_4 + H_2SO_4 = 2\,KHSO_4$$

It is a white, crystalline salt, very soluble in water.



Potassium nitrate, KNO_3, which is formed when nitric acid and potassium carbonate or potassium hydroxide act upon one another, has long been known as "niter" or "saltpeter." It is formed in the soil, by the decay of nitrogenous organic matter in the presence of soluble potassium compounds, under proper conditions of heat and moisture.

Potassium nitrate crystallizes in anhydrous prisms. It gives a cool sensation when tasted. At 340° it fuses, and at higher temperatures it gives off oxygen. For this reason it is a ready oxidizer.

Nitrification. Soils derived from feldspar minerals contain potassium salts, and in heavily wooded districts, as well as in regions long inhabited, the soil contains a layer of finely divided *humus* — derived from vegetable and animal refuse. Such soils contain also a minute vegetable organism — a *nitrifying ferment* — which helps on the process of *nitrification*. In a hot, dry climate the niter so formed will exude from the surface of the soil, forming a thin, white incrustation. For many years the world's supply of the salt was gathered and crystallized from the soils of inhabited regions in India and other Eastern countries. Niter is a constituent of gunpowder, and when the demand for gunpowder arose, the manufacture of niter by an artificial reproduction of the natural process, in *niter plantations*, was undertaken in Europe. Compact heaps of decomposing animal refuse, wood ashes, and plaster were protected from the rain and left to the action of the air for two or three years, and finally treated with water and potassium carbonate.

More recently the German process, which utilizes the Stassfurt deposits of potassium chloride and the sodium nitrate from South America, has superseded the old process. When these two salts are brought together in solution under certain conditions of temperature and pressure, a metathesis takes place. When the mixture is cooled, the sodium chloride crystallizes out and settles to the bottom and the potassium nitrate solution can be decanted.

$$KCl + NaNO_3 = KNO_3 + NaCl$$

K — Cl *Potassium chloride*, KCl, made by the interaction of hydrochloric acid and potassium carbonate or potassium hydroxide, is found in sea water and in salt deposits. The Stassfurt mines, the largest salt beds in the world, yield many thousands of tons of potassium chloride annually. Potassium chloride crystallizes in white anhydrous cubes, easily soluble in water. It is used in making other salts of potassium. It occurs as the mineral *sylvite*, KCl, and as a constituent of *carnallite*, $MgCl_2 \cdot KCl \cdot 6\,H_2O$.

Potassium. *Potassium* was first prepared by Davy, in 1807, by the electrolysis of potassium hydroxide.

$$\begin{array}{l} K-O-H \\ K-O-H \end{array} = \begin{array}{l} K \\ K \end{array} + H-H + O=O$$

It may also be made by reducing potassium carbonate by carbon at high heat. This is the commercial method for the production of potassium. The mixture of carbon and potassium carbonate is heated in an iron retort, the resulting vapors are condensed in receivers of peculiar construction, and the metal is collected and kept under petroleum.

Potassium is a silvery white, lustrous metal, very soft, of specific gravity 0.87, melting at 62°, and boiling at 667°, forming a greenish vapor at red heat. It oxidizes spontaneously in air, and burns when ignited. It decomposes water spontaneously with evolution of hydrogen, and so much heat is evolved in the reaction that the gas inflames.

Potassium Oxides. On heating potassium in oxygen a yellow mass is formed, which is a mixture of *potassium dioxide*, K_2O_2, and *potassium tetroxide*, K_2O_4. At high temperatures these oxides lose oxygen, and a white substance is formed, having a composition approaching that of *potassium monoxide*, K_2O, though this oxide is not known in a state of purity.

Spectrum. The potassium salts color the Bunsen flame violet and exhibit in the spectroscope a characteristic spectrum which consists of two red lines and a violet line.

Summary. *In regard to the potassium compounds, we note that the potassium salts, white and soluble, may be made by acting with acids upon the commercial potassium carbonate, or upon the strongly basic potassium hydroxide, which may be made by treating potassium carbonate with lime. Potassium, formed by electrolysis of potassium hydroxide, combines with oxygen to form potassium dioxide and potassium tetroxide. The potassium salts give in the Bunsen flame a violet color and a spectrum consisting of two red lines and a violet line.*

RUBIDIUM, Rb, 85.5

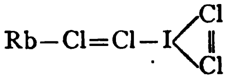
The compounds of rubidium are widely but very sparingly diffused in rocks, soils, and mineral waters. The mineral *lepidolite* sometimes carries as much as 0.5 per cent. of the element, and is the material from which rubidium salts are most easily prepared. From the mass of alkali salts left after treatment of the mineral, a pure rubidium salt may be prepared, by taking advantage of the relatively different insolubilities of the chlorplatinates of the alkali metals, R_2PtCl_6, or of the different solubilities of the double sulphates or alums, $KAl(SO_4)_2 \cdot 12\ H_2O$.

From either of these pure salts other compounds of rubidium may be prepared. From fused rubidium chloride the metal may be obtained by electrolysis, and by heating rubidium hydroxide with magnesium in an iron tube in an atmosphere of hydrogen, rubidium may be distilled and collected under petroleum.

Rubidium is a silvery yellowish white metal of specific gravity 1.52 and melting point 38.5°, easily oxidized in the air and reactive with water at ordinary temperatures with formation of hydrogen and ***rubidium hydroxide***, $RbOH$, a base from which many salts may be prepared in which rubidium acts as a univalent positive ion.

Characteristic soluble compounds of rubidium are the ***rubidium hydroxide***, $RbOH$; ***rubidium chloride***, $RbCl$; ***rubidium nitrate***, $RbNO_3$; ***rubidium sulphate***, Rb_2SO_4; ***rubidium hydrogen sulphate***, $RbHSO_4$, ***rubidium carbonate***, Rb_2CO_3. Some fairly insoluble salts are ***rubidium chlorplatinate***, Rb_2PtCl_6; ***rubidium perchlorate***, $RbClO_4$; ***rubidium hydrogen tartrate***, $RbHC_4H_4O_6$; with which should be mentioned the difficultly soluble and crystallizable ***rubidium aluminium sulphate***, $RbAl(SO_4)_2 \cdot 12\ H_2O$, an alum. ***Rubidium tetroxide***, Rb_2O_4, which is formed when rubidium burns in air, yields with water ***rubidium hydroxide***, $RbOH$, corresponding to the unknown oxide Rb_2O.

Beside the compounds in which rubidium acts unmistakably as a univalent positive ion, certain compounds of rubidium, formed by adding chlorine, bromine, or iodine, the so-called "halogens," to solutions of the halogen salts, present interesting relations. In such compounds as $RbClBr_2$, $RbBr_3$, $RbCl_4I$, which suggest at first sight the polyvalence of rubidium, rubidium may still be regarded as univalent; *e.g.* $RbCl \cdot ICl_3$, or



$$Rb-Cl=Cl-I\begin{matrix}Cl\\ \| \\ Cl\end{matrix}$$

Double halogen salts of rubidium and other metals, such as $RbCl \cdot SbCl_3$, $RbBr \cdot PbBr_2$, $RbI \cdot TlI_3 \cdot 2\ H_2O$, and many others of greater complexity, are known.

Rubidium salts give a violet color in the Bunsen flame, and exhibit a spectrum consisting of two very characteristic violet lines associated with two less prominent dark red lines lying near the red line of potassium and other lines less important.

CÆSIUM, Cs, 132.9

The compounds of cæsium occur widely disseminated with salts of the other alkali elements in rocks, soil, and waters, but with rare exceptions are present in extremely small amounts. The rare mineral *pollucite*, a silicate, contains cæsium to nearly a third of its weight, and from it pure cæsium salts may be prepared. The addition of antimony trichloride, $SbCl_3$, to the solution of alkali chlorides obtained by treatment of pollucite with hydrochloric acid, effects the precipitation of the double salt $3\ CsCl \cdot 2\ SbCl_3$, which may be decomposed by boiling with dilute ammonia. Upon removal of the insoluble antimony trioxide by filtration, and the ammonium chloride by ignition, cæsium chloride remains, from which by suitable means other compounds of cæsium may be prepared.

Cæsium, best obtained by heating in an iron tube a mixture of cæsium hydroxide and magnesium, is silvery white, the most electro-positive of the metals, of specific gravity 1.85 and melting point 25.6°, oxidizable and inflammable in air after short exposure, and reacting with water at ordinary temperatures forming hydrogen and cæsium hydroxide, the base of many salts in which cæsium acts as a univalent positive ion.

Characteristic soluble compounds of cæsium are *cæsium hydroxide*, $CsOH$; *cæsium chloride*, $CsCl$; *cæsium nitrate*, $CsNO_3$; *cæsium sulphate*, $CsSO_4$; *cæsium hydrogen sulphate*, $CsHSO_4$; and *cæsium carbonate*, Cs_2CO_3. Among the fairly insoluble salts are *cæsium chlorplatinate*, Cs_2PtCl_6; the double cæsium and antimony chloride, $3\,CsCl \cdot 2\,SbCl_3$ (in presence of sufficient hydrochloric acid); the double cæsium and lead chloride, $2\,CsCl \cdot PbCl_4$; and the *cæsium aluminium sulphate*, $CsAl(SO_4)_2 \cdot 12\,H_2O$, an alum.

Highly characteristic is the property exhibited by cæsium salts of the halogens to form with free halogens many salts in which cæsium apparently shows a valence of III or V, but these compounds are in all probability best explained as salts of the simple cæsium halogen salts combined with complexes of the halogens. As types of such salts may be taken $CsBr_3$, CsI_5, $CsBr_3I_2$. Complex double halogen salts, like $CsCl \cdot AgCl$, $CsBr \cdot PbBr_2$, $CsI \cdot CdI_2 \cdot H_2O$, and many others, have been studied.

Salts of cæsium color the Bunsen flame violet with production of a spectrum characterized by two brilliant blue lines.

CHAPTER V

PRIMARY SERIES — GROUP II

GLUCINUM (BERYLLIUM), Gl, 9.1
Magnesium, Mg, 24.36
Calcium, Ca, 40.1
Strontium, Sr, 87.6
Barium, Ba, 137.4
RADIUM, Ra, 225

Group II: Alkali Earth Elements.

THE elements of Group II of the primary series, with the exception of the rare element radium, are strikingly similar to one another, and are known as the *alkali earth elements* from their similarity to the alkali elements and from the fact that they form earthy oxides. They are never found free, and have only in more recent years been prepared from their compounds. They are all lustrous metals, of relatively low specific gravity, generally ductile and malleable. Glucinum is unaffected by ordinary air; magnesium is oxidized superficially in damp air; calcium, strontium, and barium oxidize readily in damp air, forming oxides. Glucinum does not decompose water; magnesium decomposes water at high temperatures; and the other metals decompose water spontaneously at ordinary temperatures, forming hydroxides. The oxides combine with water, forming hydroxides. The hydroxides of the group are all strong bases, which neutralize acids forming salts, and which dissociate when heated. The salts of the group are generally white in color, and with the exception of the sulphates and carbonates, the common salts are soluble in water. The salts of calcium, strontium, and barium give characteristic spectra. Glucinum, magnesium, calcium, barium, and strontium act as strongly positive ions in combination, and exhibit a valence of II.

Radium, an extremely rare element, quite recently discovered and never yet isolated, also appears as a bivalent positive ion in those of its salts which have been investigated.

Rocks. The compounds of the more important elements of the group are found associated with the alkali elements in the mineral constituents of many *rocks* and in soils produced by the weathering of rocks. The many varieties of *limestone*, deposited as strata in ancient sea beds, consist essentially of the mineral *calcite*, $CaCO_3$, colored by compounds of iron and other elements. *Dolomite*, or "dolomitic limestone," contains the mineral *magnesite*, $MgCO_3$, combined with calcite. *Marble* is a crystalline rock consisting of calcite, $CaCO_3$, either pure or colored by compounds of iron and other elements. Calcium carbonate is also found in deposits of *chalk*, in the *stalactites* and *stalagmites* of caverns, and as *coral* and *shells*. The sea water and the waters of many mineral springs contain the chlorides and sulphates of magnesium and of calcium, and by the evaporation of such waters these salts are left behind in dry deposits. The Stassfurt salt beds contain *carnallite*, $KCl \cdot MgCl_2 \cdot 6\,H_2O$, *kieserite* $MgSO_4 \cdot H_2O$, and *anhydrite*, $CaSO_4$.

Limestone.

The compounds of barium and strontium are found, associated more or less with magnesium and calcium, in a few minerals. Strontium is found in *celestite*, $SrSO_4$, and *strontianite*, $SrCO_3$, and barium in *barite*, $BaSO_4$ (heavy spar), and *witherite*, $BaCO_3$. Glucinum occurs in the complex mineral *beryl*, $6\,GlO \cdot 2\,Al_2O_3 \cdot 12\,SiO_2 \cdot H_2O$.

Radium compounds are found in very minute quantities in certain complex native compounds of uranium.

GLUCINUM (BERYLLIUM), Gl, 9.1

The chief natural compound of glucinum or beryllium is the mineral *beryl*, $6\,GlO \cdot 2\,Al_2O_3 \cdot 12\,SiO_2 \cdot H_2O$, a silicate of glucinum and aluminium. By fusing finely pulverized beryl with potassium fluoride and treating the resulting material with sulphuric acid, the silicon is volatilized as silicon fluoride, and from the solution of the residue the larger part of the aluminium may be crystallized out as potassium aluminium sulphate, or alum, $KAl(SO_4)_2 \cdot 12\,H_2O$. From the residue the remainder of the aluminium and traces of iron and other foreign elements may be precipitated by ammonium carbonate, and from the solution, after filtering and acidulating with hydrochloric acid, ammonium hydroxide precipitates glucinum hydroxide, $Gl(OH)_2$, from which many salts, in most of which glucinum acts as a bivalent positive ion, may be prepared. From *glucinum hydroxide*, $Gl(OH)_2$, sodium hydroxide, $NaOH$, and hydrofluoric acid, HF, a double fluoride of glucinum and sodium, $NaF \cdot GlF_2$, may be prepared, which upon electrolysis yields elementary glucinum.

Glucinum is a white, ductile metal of specific gravity 1.8, resisting oxidation in the air at ordinary temperatures and without action upon water even at the boiling temperature, attacked readily by hydrochloric acid forming *glucinum chloride*, $GlCl_2$, and in solution by sulphuric acid, forming *glucinum sulphate*, $GlSO_4$, and also attacked by sodium hydroxide and by potassium hydroxide, with evolution of hydrogen.

Glucinum oxide, GlO, the only known oxide of glucinum, is a white powder obtained by igniting *glucinum hydroxide*, $Gl(OH)_2$, but difficultly acted upon by acids after ignition.

Glucinum hydroxide, $Gl(OH)_2$, white and gelatinous, is precipitated by ammonium hydroxide from solutions of salts in which glucinum is the positive ion, and by dilution and boiling from solutions in which glucinum is the negative ion, as in the solutions obtained by acting upon the metal or the hydroxide with sodium hydroxide or potassium hydroxide.

Glucinum chloride, $GlCl_2$, sublimed in white needles when glucinum oxide is ignited with carbon in a current of chlorine, dissolves in water, and upon evaporating the solution, crystals are obtained of the hydrous glucinum chloride, $GlCl_2 \cdot 4\ H_2O$, which is also obtained by dissolving glucinum hydroxide in hydrochloric acid. This salt is, however, decomposed hydrolytically with evolution of hydrogen chloride if the attempt be made to render it anhydrous by heating.

Glucinum sulphate, $GlSO_4$, crystallizes from water as $GlSO_4 \cdot 7\ H_2O$ or $GlSO_4 \cdot 4\ H_2O$, which leaves $GlSO_4 \cdot 2\ H_2O$ at 105°, and at 250°–260° forms the anhydrous salt, $GlSO_4$.

Glucinum carbonate, $GlCO_3 \cdot 4\ H_2O$, forms in colorless crystals when glucinum hydroxide, $Gl(OH)_2$, suspended in water, is treated with an excess of carbon dioxide, and the solution evaporated over sulphuric acid in an atmosphere of carbon dioxide. On exposure, carbon dioxide escapes, and a basic carbonate is formed; and a basic carbonate $2\ Gl(OH)_2 \cdot GlCO_3 \cdot 3\ H_2O$ is precipitated when the solution of a glucinum salt is treated with an alkali carbonate and boiled. Glucinum shows a strong tendency to form under favorable conditions other basic salts, for example, basic sulphates and basic nitrates.

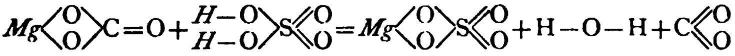
The salts of glucinum have a sweet taste, which suggested the name of the element.

Magnesium, Mg, 24.36

Magnesium Carbonate. We may commence the study of the magnesium compounds with *magnesium carbonate*, $MgCO_3$, the principal native compound of magnesium, which in its compact native form is insoluble in water, but may be attacked by fairly concentrated acids.

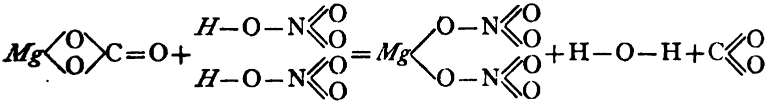
Both basic carbonates and acidic carbonates of magnesium, more readily acted upon by acids, may be formed as precipitates. When to a solution of a magnesium salt a soluble carbonate, such as sodium carbonate, Na_2CO_3, is added, a precipitate is formed which varies in composition according to the temperatures and conditions of action. The neutral magnesium carbonate, $MgCO_3$, containing water of crystallization, may be precipitated at low temperatures, while at high temperatures carbon dioxide escapes and a basic carbonate is formed. One of the basic magnesium carbonates which may thus be prepared by precipitation and drying is the *magnesia alba* of medicine, and has the composition $Mg_4(OH)_2(CO_3)_3 \cdot 4\ H_2O$. Both the neutral and the basic carbonates of magnesium are acted upon by an excess of carbon dioxide, forming a solution of an acidic magnesium carbonate, $MgH_2(CO_3)_2$, which is used in medicine under the name of *fluid magnesia*, and from which, by spontaneous loss of carbon dioxide, the crystallized neutral carbonates, $MgCO_3 \cdot 3\ H_2O$ and $MgCO_3 \cdot 5\ H_2O$, may be obtained.

Magnesium Carbonates and Acids. *The magnesium carbonates are acted upon by acids with evolution of carbon dioxide and formation of salts in which magnesium is the positive ion.* Thus, when magnesium carbonate, $MgCO_3$, is acted upon by sulphuric acid, carbon dioxide escapes, and *magnesium sulphate*, $MgSO_4$, is produced in solution.



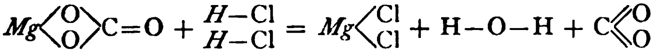
$$Mg{<}\begin{matrix}O\\O\end{matrix}{>}C=O+\begin{matrix}H-O\\H-O\end{matrix}{>}S{<}\begin{matrix}O\\O\end{matrix}=Mg{<}\begin{matrix}O\\O\end{matrix}{>}S{<}\begin{matrix}O\\O\end{matrix}+H-O-H+C{<}\begin{matrix}O\\O\end{matrix}$$

When the magnesium carbonate is decomposed by nitric acid, *magnesium nitrate*, $Mg(NO_3)_2$, is formed in solution.



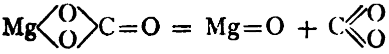
$$Mg{<}\begin{matrix}O\\O\end{matrix}{>}C=O+\begin{matrix}H-O-N{<}\begin{matrix}O\\O\end{matrix}\\H-O-N{<}\begin{matrix}O\\O\end{matrix}\end{matrix}=Mg{<}\begin{matrix}O-N{<}\begin{matrix}O\\O\end{matrix}\\O-N{<}\begin{matrix}O\\O\end{matrix}\end{matrix}+H-O-H+C{<}\begin{matrix}O\\O\end{matrix}$$

When hydrochloric acid is employed to effect the decomposition, *magnesium chloride*, $MgCl_2$, is obtained in solution.



$$Mg{<}\begin{matrix}O\\O\end{matrix}{>}C=O+\begin{matrix}H-Cl\\H-Cl\end{matrix}=Mg{<}\begin{matrix}Cl\\Cl\end{matrix}+H-O-H+C{<}\begin{matrix}O\\O\end{matrix}$$

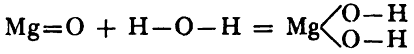
Magnesium Oxide and Hydroxide. When magnesium carbonate, $MgCO_3$, is heated to 300°, it loses carbon dioxide, and a residue remains of white *magnesium oxide*, MgO (magnesia), which may be either light and feathery, or heavy and compact, according to the mode of preparation.



$$Mg{<}\begin{matrix}O\\O\end{matrix}{>}C=O=Mg=O+C{<}\begin{matrix}O\\O\end{matrix}$$

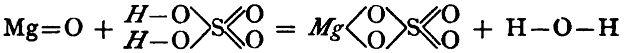
The basic magnesium carbonates decompose in a similar manner when heated, carbon dioxide and water being evolved, and a residue of magnesium oxide being left behind. Magnesium oxide is very infusible, and glows brightly when heated.

Magnesium oxide, MgO, combines with water more or less rapidly, according to the degree of ignition employed in its preparation, forming white anhydrous *magnesium hydroxide*, $Mg(OH)_2$, which is slightly soluble in water, and acts as a base.

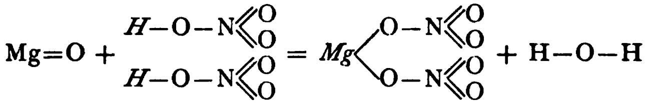


Magnesium hydroxide may also be formed as a precipitate by adding a soluble hydroxide to a solution of a magnesium salt. When gently heated, magnesium hydroxide decomposes into magnesium oxide and water. It will absorb carbon dioxide from the air, forming a magnesium carbonate. It occurs native as the mineral *brucite*.

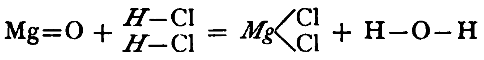
Magnesium oxide may be acted upon by acids with formation of magnesium salts. By the action of sulphuric acid upon magnesium oxide we obtain *magnesium sulphate*, $MgSO_4$.



If we use nitric acid, we obtain *magnesium nitrate*, $Mg(NO_3)_2$.

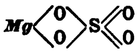


If hydrochloric acid is employed, *magnesium chloride*, $MgCl_2$, is obtained.

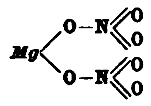


Magnesium hydroxide also neutralizes acids to form corresponding salts.

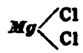
Soluble Magnesium Salts. By the action of the common acids upon magnesium carbonate, magnesium hydroxide, magnesium oxide, or magnesium, salts of magnesium are formed, which are generally white in color and soluble in water.



Magnesium sulphate, $MgSO_4$, which, as we have seen, may be formed by the action of sulphuric acid upon magnesium carbonate or hydroxide or oxide, and, as will appear later, can also be made by the action of the same acid upon magnesium, may be obtained from its solution by spontaneous evaporation at ordinary temperature. It forms colorless rhombic crystals of the composition $MgSO_4 \cdot 7\ H_2O$. These crystals have a bitter salty taste and are used in medicine under the name *Epsom salts*. The proportionate amount of water held in the crystals varies with the temperature, the composition of the salt at 70° being $MgSO_4 \cdot 7\ H_2O$, while at 0° it is $MgSO_4 \cdot 12\ H_2O$, and at 150° $MgSO_4 \cdot H_2O$. At 200° it is anhydrous. It is found in mineral springs and in sea water, and in the Stassfurt deposits as the mineral *kieserite*.



Magnesium nitrate, $Mg(NO_3)_2$, may be obtained as a colorless deliquescent substance by the action of nitric acid upon magnesium carbonate, or oxide, or upon magnesium.



$Mg\begin{smallmatrix}/Cl\\ \backslash Cl\end{smallmatrix}$

Magnesium chloride, $MgCl_2$, formed by the action of hydrochloric acid upon magnesium carbonate or magnesium hydroxide or oxide, or upon magnesium, may be recovered from its solutions as colorless deliquescent crystals having the composition $MgCl_2 \cdot 6\ H_2O$. When these are heated, part of the water of crystallization is removed, and the remaining water causes the hydrolysis of some of the magnesium chloride.

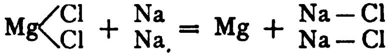
$$Mg\begin{smallmatrix}/Cl\\ \backslash Cl\end{smallmatrix} + H-O-H = Mg=O + \begin{matrix}H-Cl\\ H-Cl\end{matrix}$$

Magnesium chloride forms many double salts with other compounds, and from the double salt ammonium magnesium chloride, $MgCl_2 \cdot NH_4Cl \cdot 6\ H_2O$, anhydrous magnesium chloride may be obtained by ignition. Magnesium chloride is found in mineral springs and in sea water, in which it constitutes one sixth of the dissolved solid matter. At Stassfurt it occurs as a constituent of *carnallite*, $MgCl_2 \cdot KCl \cdot 6\ H_2O$. It is a common impurity in natural sodium chloride (salt), where it is deleterious because of its hygroscopic properties.

Magnesium. *Magnesium may be prepared by the electrolysis of magnesium chloride.* When fused magnesium chloride, $MgCl_2$, or carnallite, $MgCl_2 \cdot KCl \cdot 6\ H_2O$, is subjected to electrolysis, dissociation takes place, and magnesium is liberated.

$$Mg\begin{smallmatrix}/Cl\\ \backslash Cl\end{smallmatrix} = Mg + Cl-Cl$$

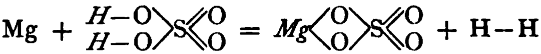
A similar liberation of magnesium takes place when magnesium chloride, best when mixed with a chloride of an alkali element, or when in a double chloride, is heated with sodium.



$$\mathrm{Mg}\begin{matrix}\diagup\mathrm{Cl}\\ \diagdown\mathrm{Cl}\end{matrix} + \begin{matrix}\mathrm{Na}\\ \mathrm{Na}\end{matrix} = \mathrm{Mg} + \begin{matrix}\mathrm{Na-Cl}\\ \mathrm{Na-Cl}\end{matrix}$$

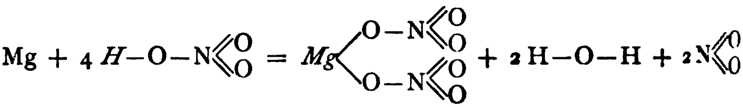
Magnesium is a brilliant white metal. It is hard, and both malleable and ductile. It has a specific gravity of 1.74. It melts at about 700°. It scarcely oxidizes at all in the air at ordinary temperatures, but when ignited it burns, emitting an extremely brilliant white light, useful in photography and in fireworks. Its strong affinity for oxygen makes it a valuable reducer for some oxides and acids. It slowly decomposes boiling water, forming the insoluble hydroxide which tends to incrust the magnesium and thus stop the action.

Magnesium is readily acted upon by dilute acids with the formation of the corresponding magnesium salts. When, for example, a piece of magnesium ribbon is acted upon by dilute sulphuric acid, magnesium sulphate is produced in solution, while hydrogen is liberated.



$$\mathrm{Mg} + \begin{matrix}H\mathrm{-O}\diagdown\\ H\mathrm{-O}\diagup\end{matrix}\mathrm{S}\begin{matrix}\diagup\!\!\diagup\mathrm{O}\\ \diagdown\!\!\diagdown\mathrm{O}\end{matrix} = Mg\begin{matrix}\diagup\mathrm{O}\diagdown\\ \diagdown\mathrm{O}\diagup\end{matrix}\mathrm{S}\begin{matrix}\diagup\!\!\diagup\mathrm{O}\\ \diagdown\!\!\diagdown\mathrm{O}\end{matrix} + \mathrm{H-H}$$

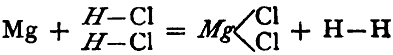
When, however, magnesium reacts with dilute nitric acid, the higher oxides of nitrogen, of dark color and characteristic odor, are given off, and magnesium nitrate remains dissolved.



$$\mathrm{Mg} + 4\,H\mathrm{-O-N}\begin{matrix}\diagup\!\!\diagup\mathrm{O}\\ \diagdown\mathrm{O}\end{matrix} = Mg\begin{matrix}\diagup\mathrm{O-N}\begin{matrix}\diagup\!\!\diagup\mathrm{O}\\ \diagdown\mathrm{O}\end{matrix}\\ \diagdown\mathrm{O-N}\begin{matrix}\diagup\!\!\diagup\mathrm{O}\\ \diagdown\mathrm{O}\end{matrix}\end{matrix} + 2\,\mathrm{H-O-H} + 2\,\mathrm{N}\begin{matrix}\diagup\!\!\diagup\mathrm{O}\\ \diagdown\mathrm{O}\end{matrix}$$

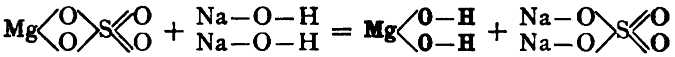
It should be noticed that although in many cases hydrogen is evolved by the action of an acid upon a metal, in the case of nitric acid the hydrogen, when set free, immediately accomplishes the decomposition of some of the excess of nitric acid present, forming water and liberating nitrogen oxides. Only in very rare cases is hydrogen evolved in the action of nitric acid upon a metal.

Hydrochloric acid readily acts upon magnesium, forming magnesium chloride and liberating hydrogen.



$$\mathrm{Mg} + \begin{matrix}H\mathrm{-Cl}\\ H\mathrm{-Cl}\end{matrix} = Mg\begin{matrix}\diagup\mathrm{Cl}\\ \diagdown\mathrm{Cl}\end{matrix} + \mathrm{H-H}$$

Insoluble Magnesium Compounds. *The formation of certain insoluble magnesium compounds as precipitates furnishes a ready means for the identification of magnesium compounds in solution.* For example, when we add to a solution of a magnesium compound such as magnesium sulphate, $MgSO_4$, a soluble hydroxide, such as sodium hydroxide, NaOH, we get a white gelatinous mass of *magnesium hydroxide*, $Mg(OH)_2$.

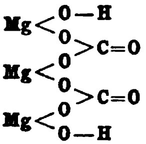


$$Mg\left\langle\begin{matrix}O\\O\end{matrix}\right\rangle S\left\langle\begin{matrix}O\\O\end{matrix}\right. + \begin{matrix}Na-O-H\\Na-O-H\end{matrix} = Mg\left\langle\begin{matrix}O-H\\O-H\end{matrix}\right. + \left.\begin{matrix}Na-O\\Na-O\end{matrix}\right\rangle S\left\langle\begin{matrix}O\\O\end{matrix}\right.$$

The precipitate is attacked by ammonium salts, forming double salts of ammonium and magnesium. Thus, ammonium chloride, NH_4Cl, acts upon the precipitate, forming $MgCl_2 \cdot 2\,(NH_4)Cl$.

$$Mg(OH)_2 + 4\,(NH_4)Cl = MgCl_2 \cdot 2\,(NH_4)Cl + 2\,NH_4OH$$

For this reason it is evident that in case ammonium hydroxide, NH_4OH, is used to form magnesium hydroxide, $Mg(OH)_2$, the precipitation will be only partial since the reaction is reversible.



When to a solution of magnesium sulphate a soluble carbonate is added, such as sodium carbonate, Na_2CO_3, a white precipitate of a magnesium carbonate is produced, the composition of which depends upon the proportions of the reagents and the temperature under which the action takes place. The *basic magnesium carbonate* precipitated from boiling solutions, $Mg_3(OH)_2(CO_3)_2$, may serve as a type of similar salts.

$$3\,MgSO_4 + 3\,Na_2CO_3 + H_2O = Mg_3(OH)_2(CO_3)_2 + 3\,Na_2SO_4 + CO_2$$

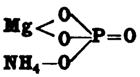
If ammonium carbonate, $(NH_4)_2CO_3$, instead of sodium carbonate, is added to the solution of a magnesium salt, the precipitation is only partial, and if ammonium chloride, NH_4Cl, be also present in sufficient amount, no precipitation takes place, a soluble double salt of magnesium and "ammonium" being formed in both cases.

The precipitated basic magnesium carbonate, $Mg_3(OH)_2(CO_3)_2$, is readily acted upon by dilute acids with the liberation of carbon dioxide and the formation in solution of a magnesium salt of the acid employed. Thus, sulphuric acid will form magnesium sulphate in solution.

$$Mg_3(OH)_2(CO_3)_2 + 3\,H_2SO_4 = 3\,MgSO_4 + 4\,H_2O + 2\,CO_2$$

The basic magnesium carbonate, $Mg_3(OH)_2(CO_3)_2$, is readily decomposed by heat, with the liberation of carbon dioxide and the formation of a residue of magnesium oxide which remains unaffected by further heating and which gives rise to no effervescence with acids.

$$Mg_3(OH)_2(CO_3)_2 = 3\,MgO + H_2O + 2\,CO_2$$



The magnesium phosphates may be readily formed from solutions of magnesium salts. Thus, the common sodium phosphate, Na_2HPO_4, will give magnesium phosphate, $Mg_3(PO_4)_2$, a white flocculent precipitate not particularly characteristic in appearance. We may, however, get a finely crystalline characteristic white precipitate of *ammonium magnesium phosphate*, NH_4MgPO_4, by adding to a dilute solution of magnesium sulphate a solution of ammonium chloride, NH_4Cl, in excess, to prevent the subsequent precipitation of magnesium hydroxide; then ammonium hydroxide, NH_4OH, in excess; and finally disodium hydrogen phosphate, Na_2HPO_4, or sodium ammonium hydrogen phosphate, $Na(NH_4)HPO_4$ (microcosmic salt), drop by drop with constant stirring, until the reagent is present in excess, and the precipitation, which proceeds somewhat slowly, stops altogether.

$$MgSO_4 + Na_2HPO_4 + NH_4OH = \mathbf{Mg(NH_4)PO_4} + Na_2SO_4 + H_2O$$

The precipitate is slightly soluble in water, but unacted upon by ammonium hydroxide. It is readily acted upon by ordinary acids, and from the solutions thus formed it may be reprecipitated by the addition of ammonium hydroxide. Thus, it is acted upon by sulphuric acid with the formation of magnesium sulphate, and ammonium sulphate, $(NH_4)_2SO_4$, in solution, and phosphoric acid, H_3PO_4, which also remains dissolved.

$$2\,Mg(NH_4)PO_4 + 3\,H_2SO_4 = 2\,MgSO_4 + (NH_4)_2SO_4 + 2\,H_3PO_4$$

When ammonium hydroxide, NH_4OH, is added to the solution thus obtained, the ammonium magnesium phosphate is again precipitated.

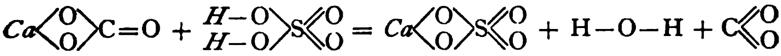
Summary. *By the action of the common acids upon the native or precipitated magnesium carbonates, or upon magnesium oxide, magnesium hydroxide, or magnesium, soluble salts may be formed. Magnesium carbonate and magnesium hydroxide decompose on heating, forming magnesium oxide. Magnesium is formed by the electrolysis of* *fused magnesium chloride, and is acted upon by acids with formation of magnesium salts. Magnesium hydroxide, basic magnesium carbonates, and magnesium ammonium phosphate may be formed as characteristic white precipitates.*

Calcium, Ca, 40.1

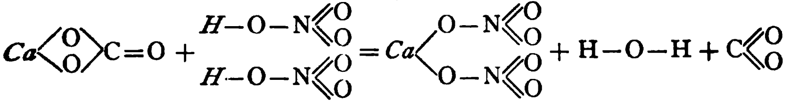
Calcium Carbonate. We may commence our study of the calcium compounds with the commonly occurring calcium carbonate, $CaCO_3$, from which the other calcium compounds may be obtained.

Calcium carbonate, $CaCO_3$, occurs commonly in pure condition as the crystallized minerals *calcite* and *aragonite*, and in impure forms as the soft *seashells*, *coral*, and *chalk*, and the hard, massive *limestones* and *marbles*. It is a white solid insoluble in water, acted upon by water charged with carbon dioxide, and readily attacked by dilute acids. It may be formed as a precipitate by adding a suitable reagent to a solution of a calcium compound.

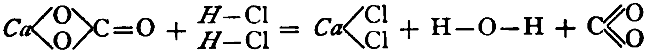
Calcium Carbonate and Acids. *Calcium carbonate is acted upon by suitable acids with formation of corresponding salts in which calcium is a positive ion.* If we act upon calcium carbonate, $CaCO_3$, with dilute sulphuric acid, there will be an effervescence of carbon dioxide, CO_2, and a residue of white *calcium sulphate*, $CaSO_4$, sparingly soluble in water, will be left behind. The action will proceed slowly because the calcium sulphate is deposited as a coating on the calcium carbonate and tends to prevent the contact of the two reacting substances.



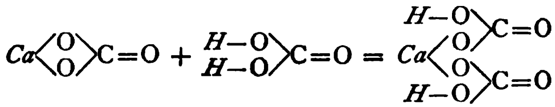
If we act similarly with dilute nitric acid, *calcium nitrate*, $Ca(NO_3)_2$, will remain dissolved in the solution.



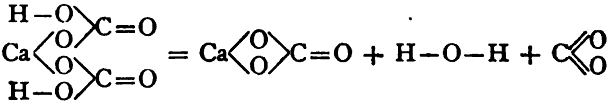
If we use hydrochloric acid, we shall get *calcium chloride*, $CaCl_2$, in solution.



When calcium carbonate is acted upon by carbon dioxide, CO_2, dissolved in water, in effect carbonic acid, H_2CO_3, *calcium hydrogen carbonate*, $CaH_2(CO_3)_2$, is formed in solution.

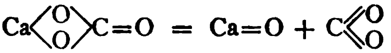


This solution loses carbon dioxide spontaneously on standing, and more rapidly on heating, with the formation and deposition of the insoluble calcium carbonate.



Calcium Oxide and Hydroxide.

When calcium carbonate is heated to redness, it dissociates, carbon dioxide, CO_2, being evolved and a residue of *calcium oxide*, CaO, or *quicklime*, being left behind.



In a closed space this reaction may be incomplete and reversible.

$$CaCO_3 \rightleftarrows CaO + CO_2$$

The conditions of equilibrium depending upon temperature and pressure, between the solid phase CaO, the gaseous phase CO_2, and the solid phase $CaCO_3$, made up of the components CaO and CO_2, are shown qualitatively in the diagram. For temperatures and pressures represented by individual points below the line *AB*, the two phases CaO and CO_2 exist in equilibrium; for temperatures and pressures represented by single points above the line *AB* the two phases $CaCO_3$ and CaO, or the two phases $CaCO_3$ and CO_2 may exist in equilibrium; while every point in the line *AB* represents a temperature and a pressure for which the three phases CaO, CO_2, and $CaCO_3$ may be in equilibrium.

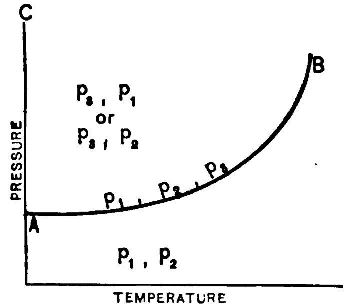
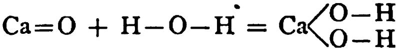


FIG. 9. — Equilibrium of Calcium Oxide, Carbon Dioxide, and Calcium Carbonate (p_1 and p_2 represent the phases CaO and CO_2 respectively; p_3 represents the phase $CaCO_3$).

Calcium oxide is a grayish white, non-crystalline solid, extremely infusible. It has been melted at 3000°, and vaporized at a higher temperature. In the *oxyhydrogen flame* it emits an intense white light which has been largely employed for illuminating purposes as the so-called "calcium light."

In the air, calcium oxide attracts moisture gradually, breaking down into a voluminous white powder which is *calcium hydroxide*, $Ca(OH)_2$, known ordinarily as *slaked lime*. When water is added directly to calcium oxide, CaO, the two substances combine with the evolution of a great deal of heat.



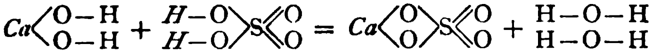
$$Ca{=}O + H{-}O{-}H = Ca\left\langle\begin{array}{l}O-H\\O-H\end{array}\right.$$

When calcium hydroxide, in dry condition, is heated to redness, it dissociates, a residue of calcium oxide being left behind.

Calcium hydroxide shows strongly basic properties. It is sparingly soluble in water. Its solution, known as *limewater*, is used in medicine to neutralize weak acids. The white emulsion, consisting of fine particles of slaked lime held in suspension in water, is known as *milk of lime.*

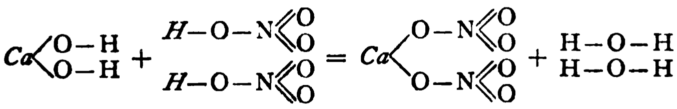
When calcium hydroxide is exposed to ordinary air, it slowly absorbs carbon dioxide, forming insoluble calcium carbonate. When calcium oxide is exposed to moist air, it first absorbs water, with the formation of calcium hydroxide, and then it gradually turns into calcium carbonate. Advantage is taken of this property of calcium oxide in making mortars and cements.

Calcium Hydroxide and Acids. *Calcium hydroxide, made by combining calcium oxide with water, is readily neutralized by acids, with formation of the corresponding calcium salts.* Thus, by acting upon the somewhat soluble calcium hydroxide, $Ca(OH)_2$, with sulphuric acid, the sparingly soluble *calcium sulphate*, $CaSO_4$, is formed.



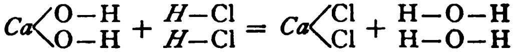
$$Ca\left\langle\begin{array}{l}O-H\\O-H\end{array}\right. + \begin{array}{l}H-O\\H-O\end{array}\!\!>S\left\langle\begin{array}{l}O\\O\end{array}\right. = Ca\left\langle\begin{array}{l}O\\O\end{array}\right.\!\!>S\left\langle\begin{array}{l}O\\O\end{array}\right. + \begin{array}{l}H-O-H\\H-O-H\end{array}$$

In a similar manner, nitric acid gives soluble *calcium nitrate*, $Ca(NO_3)_2$.



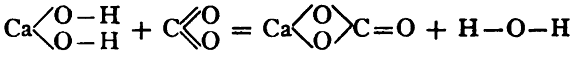
$$Ca\left\langle\begin{array}{l}O-H\\O-H\end{array}\right. + \begin{array}{l}H-O-N\left\langle\begin{array}{l}O\\O\end{array}\right.\\H-O-N\left\langle\begin{array}{l}O\\O\end{array}\right.\end{array} = Ca\left\langle\begin{array}{l}O-N\left\langle\begin{array}{l}O\\O\end{array}\right.\\O-N\left\langle\begin{array}{l}O\\O\end{array}\right.\end{array}\right. + \begin{array}{l}H-O-H\\H-O-H\end{array}$$

Hydrochloric acid forms *calcium chloride*, $CaCl_2$.



$$Ca\begin{array}{l}\diagup O-H\\ \diagdown O-H\end{array} + \begin{array}{l}H-Cl\\ H-Cl\end{array} = Ca\begin{array}{l}\diagup Cl\\ \diagdown Cl\end{array} + \begin{array}{l}H-O-H\\ H-O-H\end{array}$$

Carbonic acid, H_2CO_3, forms *calcium carbonate*, $CaCO_3$. Thus, when a current of carbon dioxide, CO_2, is passed through a solution of calcium hydroxide, a white precipitate of *calcium carbonate*, $CaCO_3$, is formed.



$$Ca\begin{array}{l}\diagup O-H\\ \diagdown O-H\end{array} + C\begin{array}{l}\diagup\!\!\diagup O\\ \diagdown\!\!\diagdown O\end{array} = Ca\begin{array}{l}\diagup O\diagdown\\ \diagdown O\diagup\end{array}C=O + H-O-H$$

The same reaction takes place when *limewater* is exposed to air containing carbon dioxide, the calcium carbonate forming an incrustation on the surface of the limewater; so, when air charged with carbon dioxide, such as air forced out from the lungs, is passed into limewater, the precipitation causes the well-known turbidity that is commonly taken as an indication of the presence of carbon dioxide.

Natural Waters and Limestone. An excess of carbon dioxide, in solution, acts upon the precipitated calcium carbonate to form calcium hydrogen carbonate, $CaH_2(CO_3)_2$, in solution.

$$CaCO_3+CO_2+H_2O=CaH_2(CO_3)_2$$

When to a solution containing the calcium hydrogen carbonate an excess of calcium hydroxide is added, a precipitate of calcium carbonate is formed,

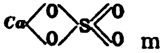
$$CaH_2(CO_3)_2+Ca(OH)_2=2\ CaCO_3+2\ H_2O$$

and if the solution of calcium hydrogen carbonate is heated, calcium carbonate is deposited.

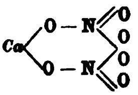
$$CaH_2(CO_3)_2=CaCO_3+H_2O+CO_2$$

The action of carbon dioxide in natural waters upon limestones sometimes produces underground passages and caverns, which often occur extensively in limestone regions. With the calcium hydrogen carbonate thus formed in solution, ordinary soap reacts with the formation of a sticky insoluble calcium soap, and loses its cleansing properties. Such "hard" waters are called "temporarily hard" because they may be softened by the addition of a measured quantity of slaked lime, causing the precipitation of calcium carbonate, or by simply boiling the water until the soluble acidic carbonate is converted to the insoluble neutral carbonate, which may be settled out, leaving clear water. The precipitation of calcium carbonate from hard waters shows how "boiler scale" is formed in vessels in which such water is kept boiling. When waters containing calcium hydrogen carbonate evaporate slowly, calcium carbonate is deposited in crystalline condition. This is the way in which such waters, penetrating the roofs of underground caverns, and dropping and evaporating, form the pendent *stalactites*, and build up *stalagmites* from the floors. Some underground mineral waters upon coming to the surface deposit limestone by a similar process.

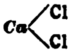
Soluble Calcium Salts. *The common calcium salts, made by the action of acids upon calcium carbonate or calcium hydroxide, are generally white solids, soluble in water.*



Calcium sulphate, $CaSO_4$, as we have observed, may be made by acting upon calcium carbonate or calcium oxide with sulphuric acid. It is a white solid only moderately soluble in water. It occurs naturally at Stassfurt as the crystallized mineral *anhydrite*, having the composition $CaSO_4$; but its more abundant forms are the coarsely crystallized *gypsum* and the finely crystalline *alabaster*, which, like the ordinarily precipitated calcium sulphate, have the composition $CaSO_4 \cdot 2\ H_2O$. Gypsum, like limestone, occurs in vast quantities as one of the rocks of the earth's crust. When gypsum is heated to 110°, it loses water, and the nearly anhydrous residue is known as "burnt gypsum" or *plaster of Paris*. When the residue is powdered and made into a pasty mass with water, it soon recombines with water, hardening into solid rock. Because of this property gypsum is of value in making casts and moldings, and in coating or kalsomining the walls of rooms. If the gypsum is heated above 160°, however, and made completely anhydrous, it will not recombine with water. Waters containing gypsum in solution are known as "permanently hard" waters, and can be softened only by removing the water from the gypsum by distillation, or by adding some substance, such as sodium carbonate, which will form from the gypsum an insoluble compound. Gypsum is sometimes applied to soils to improve their fertility.



Calcium nitrate, $Ca(NO_3)_2$, made by the action of nitric acid upon calcium carbonate or calcium oxide, is a white solid. The anhydrous form is deliquescent. When recovered from solution by evaporation, the salt crystallizes in prisms of the composition $Ca(NO_3)_2 \cdot 4\ H_2O$. It is somewhat similar in its properties to sodium nitrate and to potassium nitrate, and like these compounds may be produced in "niter plantations" by the decay of nitrogenous matter under suitable conditions. Potassium nitrate was formerly made by treating such artificial calcium nitrate with potassium carbonate made from wood ashes.



Calcium chloride, $CaCl_2$, may be made by acting upon calcium carbonate or calcium oxide with hydrochloric acid. It may be recovered from solution in large transparent prisms which have the composition $CaCl_2 \cdot 6\ H_2O$. These deliquesce when exposed to air, and when heated melt in their water of crystallization. At 200° the crystals lose two thirds of the water, becoming $CaCl_2 \cdot 2\ H_2O$, and at higher temperatures they form a white porous anhydrous mass. The fused calcium chloride is exceedingly hygroscopic, rapidly taking up water from the air, combining with the maximum of water, and finally dissolving in a thick, sirupy liquid. This property of fused calcium chloride makes it exceedingly valuable as a dryer or *desiccator* for many gases and liquids; but since the fused chloride absorbs ammonia, forming a double salt, $CaCl_2 \cdot 8\ NH_3$, it cannot be used to dry ammonia. The crystallized calcium chloride dissolves in water with great readiness, at the same time lowering its temperature. It is useful in making *freezing mixtures* with snow or ice. Calcium chloride occurs in mineral springs and in sea water.

Insoluble Calcium Compounds.

The formation of some insoluble calcium compounds as precipitates furnishes a ready means for identifying calcium compounds in solution.

For example, when a soluble hydroxide, such as sodium hydroxide, is added to a sufficiently concentrated solution of calcium chloride, $CaCl_2$, or other calcium salt, *calcium hydroxide*, $Ca(OH)_2$, is formed.

$$CaCl_2 + 2\ NaOH = \mathbf{Ca(OH)_2} + 2\ NaCl$$

Since calcium hydroxide is moderately soluble in water, it is not precipitated in dilute solutions of calcium salts; when, however, a soluble hydroxide is added to a concentrated solution of a calcium salt, calcium hydroxide is formed as a white precipitate.

When sulphuric acid, or a soluble sulphate, like potassium sulphate, is added to a solution of calcium chloride, *calcium sulphate*, $CaSO_4$, is formed.

$$CaCl_2 + H_2SO_4 = \mathbf{CaSO_4} + 2\ HCl$$

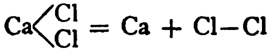
$$CaCl_2 + K_2SO_4 = \mathbf{CaSO_4} + 2\ KCl$$

Calcium sulphate is moderately soluble in water, but is insoluble in alcohol. If, therefore, it is formed in dilute solutions of calcium compounds, it appears as a precipitate either very tardily or not at all. When, however, sulphuric acid or a soluble sulphate is added to a concentrated solution of a calcium salt, the calcium sulphate appears immediately as a white crystalline precipitate. If the precipitate is removed from the liquid by filtration and alcohol is then added to the filtrate, a further precipitation of calcium sulphate takes place.

When a soluble carbonate, like sodium carbonate, is added to a solution of calcium chloride, a precipitate of white *calcium carbonate*, $CaCO_3$, forms.

$$CaCl_2 + Na_2CO_3 \doteq \mathbf{CaCO_3} + 2\,NaCl$$

Calcium. *Calcium* is a pale yellow metal of specific gravity 1.55 to 1.6, remaining nearly unchanged in dry air, but tarnishing in moist air. It decomposes water spontaneously at ordinary temperature, fuses at red heat, and while burning emits a bright yellow light. It was first obtained by Davy in 1808. It may be prepared by electrolysis of fused calcium chloride.



$$\mathrm{Ca}\begin{matrix}\diagup\mathrm{Cl}\\ \diagdown\mathrm{Cl}\end{matrix} = \mathrm{Ca} + \mathrm{Cl{-}Cl}$$

Spectrum. Compounds of calcium when volatilized impart a bright orange-red coloration to a colorless flame, and emit a complex spectrum of which one green line and one orange line are characteristic.

Summary. *By the action of the common acids upon native or precipitated calcium carbonate, or upon calcium hydroxide, calcium salts may be formed which generally are white in color and soluble, sparingly soluble, or insoluble in water. Calcium carbonate and calcium hydroxide may be decomposed by heating with formation of calcium oxide. Calcium oxide combines with water to form calcium hydroxide. By the action of carbon dioxide and water upon calcium carbonate soluble calcium hydrogen carbonate is formed which may be decomposed by heating. The sparingly soluble calcium hydroxide and calcium sulphate may be formed as white precipitates from solutions of calcium compounds sufficiently concentrated, and insoluble calcium carbonate may be precipitated from dilute solutions of calcium compounds. The calcium compounds impart an orange-red color to flame and exhibit a spectrum characterized by one green line and one orange line.*

Industrial Applications. The practical application of the compounds of calcium to the needs of daily life are many. We have mentioned the occurrence and methods of softening hard waters, and the use of gypsum in making casts and in finishing the walls of rooms, and as a fertilizer. The extensive use of limestone and marble for building material should also be noticed. In this country, much limestone comes from New York State, while the finest marble is quarried in Vermont. In Europe, the best marble is found in Italy, where it has been used for building and for sculpture since ancient times. The widespread use of limestone in making lime and the employment of the latter compound in mortar and cement are worthy of more extended discussion.

Lime. *Lime* is made on a large scale commercially by heating to redness, or "calcining," limestone, under such conditions that the carbon dioxide may readily escape as fast as it is formed. The operation takes place in a large brick or iron furnace or *lime kiln*, frequently set on a side hill to facilitate feeding in the limestone at the top. In some forms of kiln a stone archway, provided with numerous small openings, is built near the bottom, above which is piled the limestone, broken into coarse lumps, while below the arch a fire is made, so arranged that its flames may pass through the arch into the interior of the kiln. The kiln and its contents are gently heated at first, and then maintained at red heat for two or more days, when the fire is allowed to die out, the kiln is allowed to cool, and the freshly burned lime is removed. In the more modern kilns the fuel is either burned on a grate or is fed in alternately with limestone at the top, in either case the feeding of the limestone and the removal of the lime being carried on continuously without interrupting the operation of burning.

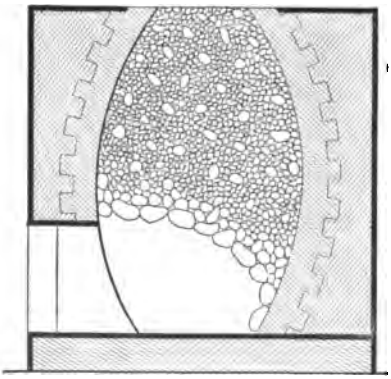


FIG. 10. — Lime Kiln. (Thorp.)

Mortar. *Mortar* is a pasty mixture of lime slaked with water (calcium hydroxide) and sand (silicon dioxide), which dries without excessive shrinkage, and which on exposure to air absorbs carbon dioxide and turns into hard, compact limestone (calcium carbonate). When a pasty mass of freshly slaked lime, unmixed with other material, is allowed to dry by exposure to air, it shrinks and cracks. If, however, a quantity of sand be mixed with the slaked lime, it prevents the shrinking, and gives to the mass a porous structure which permits the ready penetration of carbon dioxide from the air. After the application of mortar to lathing or masonry it loses water by evaporation and absorption, and partially solidifies or "sets." When perfectly dry, the absorption of carbon dioxide begins to take place slowly from the outside surface toward the interior of the mass, an action which may continue for many years. After the lapse of time a further combination may take place between the limestone and the sand, forming a hard silicate. In *cements*, which we may study more conveniently in another place, the process of hardening depends chiefly upon the hydration of silicates and aluminates of calcium.

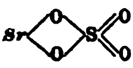
Strontium, Sr, 87.6

The strontium compounds may be made from strontium carbonate, which occurs native.

Strontium Carbonate and other Strontium Salts.

Strontium carbonate, $SrCO_3$, occurs as the mineral *strontianite*. It is nearly insoluble in water, but is acted upon by acids. It may be formed as a precipitate from solutions of other strontium salts.

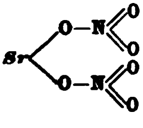
Strontium carbonate may be acted upon by acids with the formation of strontium salts in which strontium is a positive ion. When strontium carbonate, $SrCO_3$, is acted upon by sulphuric acid, some carbon dioxide, CO_2, is set free, and an equivalent amount of *strontium sulphate*, $SrSO_4$, is formed.



$$SrCO_3 + H_2SO_4 = SrSO_4 + H_2O + CO_2$$

Since, however, the strontium sulphate formed is only very slightly soluble, it forms a protective coating about the strontium carbonate and so retards, and if undisturbed, finally stops the action. Strontium sulphate occurs as the mineral *celestite*. It may be formed as a precipitate from solutions of other strontium compounds.

When strontium carbonate is acted upon by warm dilute nitric acid, carbon dioxide, CO_2, is evolved, and *strontium nitrate*, $Sr(NO_3)_2$, is left in the solution, from which it may be recovered in the form of anhydrous octahedrons, or as prisms having the composition $Sr(NO_3)_2 \cdot 4\,H_2O$.



$$SrCO_3 + 2\,HNO_3 = Sr(NO_3)_2 + H_2O + CO_2$$

When heated it breaks down into strontium oxide and nitrogen oxides. It imparts a beautiful red color to flame, and so is largely used in making fireworks.

When hydrochloric acid is used to decompose strontium carbonate, *strontium chloride*, $SrCl_2$, is formed in solution, from which it may be recovered as long, hexagonal needles, having the composition $SrCl_2 \cdot 6\ H_2O$. They effloresce in air, and when heated become anhydrous.

$$SrCO_3 + 2\ HCl = SrCl_2 + H_2O + CO_2$$

Strontium Oxide and Hydroxide.

When strontium carbonate is strongly heated, it evolves carbon dioxide, CO_2, forming *strontium oxide*, SrO (strontia), a white solid, the reaction being reversible.

$$SrCO_3 \rightleftarrows SrO + CO_2$$

Strontium oxide is more readily formed by heating strontium nitrate. It combines with water with evolution of heat, and formation of *strontium hydroxide*, $Sr(OH)_2$, a white powder, moderately soluble in hot water, and possessing basic properties, since it will neutralize acids forming corresponding strontium salts.

$$SrO + H_2O = Sr(OH)_2$$

Strontium hydroxide may be decomposed by heat into strontium oxide and water. The solution of strontium hydroxide will absorb carbon dioxide, CO_2, to form strontium carbonate.

$$Sr(OH)_2 + CO_2 = SrCO_3 + H_2O$$

When a solution of strontium hydroxide is allowed to cool, crystals separate out, having the composition $Sr(OH)_2 \cdot 8\ H_2O$.

Insoluble Compounds of Strontium.

The formation of the insoluble compounds of strontium as precipitates serves as a means for identifying the presence of strontium compounds in solution. Thus when a soluble carbonate, like sodium carbonate, is added to a solution of a strontium compound, like strontium nitrate, $Sr(NO_3)_2$, a white precipitate of *strontium carbonate*, $SrCO_3$, is formed.

$$Sr(NO_3)_2 + Na_2CO_3 = \mathbf{SrCO_3} + 2\ NaNO_3$$

When sulphuric acid, or a soluble sulphate, like potassium sulphate, is added to a solution of strontium nitrate, white, finely crystalline *strontium sulphate*, $SrSO_4$, is precipitated.

$$Sr(NO_3)_2 + H_2SO_4 = \mathbf{SrSO_4} + 2\ HNO_3$$

Since the precipitate is very slightly soluble in cold water, it is formed slowly in dilute solution.

Strontium. *Strontium* is obtained by the electrolysis of fused strontium chloride, $SrCl_2$.

$$SrCl_2 = Sr + Cl_2$$

It is a yellow metal, of specific gravity 2.5, slowly oxidizes spontaneously in air, and decomposes water at ordinary temperatures. It is malleable and ductile and fuses at red heat.

Spectrum. Strontium compounds when volatilized impart a crimson color to flame, and give a characteristic complex spectrum consisting of two red lines, one orange line, and one blue line.

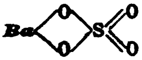
Summary. *By acting with common acids upon the native strontium carbonate, white soluble or insoluble strontium salts may be formed. Strontium carbonate and strontium hydroxide may be decomposed by heating, with formation of strontium oxide, which will combine with water to form strontium hydroxide. The sparingly soluble strontium hydroxide and the insoluble strontium sulphate and strontium carbonate may be formed as white precipitates. Strontium compounds impart a crimson color to flame, and exhibit a complex spectrum consisting of red, orange, and blue lines.*

Barium, Ba, 137.4

From barium carbonate, which occurs native, the other barium compounds may be obtained.

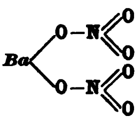
Barium Carbonate and other Barium Salts. *Barium carbonate*, $BaCO_3$, occurs as the mineral *witherite*. It is very slightly soluble in water. Its solubility is greater in water charged with carbon dioxide than in pure water. It is acted upon by acids. It may be formed as a precipitate in solutions of other barium compounds.

Barium carbonate may be acted upon by acids with the formation of barium salts in which barium is a positive ion. When barium carbonate, $BaCO_3$, is acted upon by sulphuric acid, carbon dioxide, CO_2, is evolved, and *barium sulphate*, $BaSO_4$, is deposited as a very insoluble white coating on the carbonate still undecomposed, thus retarding or completely stopping the action.



$$BaCO_3 + H_2SO_4 = BaSO_4 + H_2O + CO_2$$

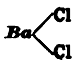
Barium sulphate is the commonest and most widely distributed compound of barium. It is found as the mineral *barite* (heavy spar). It is almost insoluble in water, and is very slightly attacked by many acids. Hot concentrated sulphuric acid acts upon it with the formation of an acidic salt, $BaH_2(SO_4)_2$, from which may be formed by action of moisture $BaH_2(SO_4)_2 \cdot 2\ H_2O$. It is largely employed in white paint. It may be formed as a precipitate from solutions of other barium compounds.



By acting upon barium carbonate with nitric acid, *barium nitrate*, $Ba(NO_3)_2$, is formed in solution, from which it may be recovered by evaporation in anhydrous crystals.

$$BaCO_3 + 2\ HNO_3 = Ba(NO_3)_2 + H_2O + CO_2$$

When heated it breaks down into barium oxide and nitrogen oxides. It is used for the preparation of barium oxide and barium dioxide. It imparts a fine green color to flame, and is employed in making fireworks.



When barium carbonate is acted upon by hydrochloric acid, *barium chloride*, $BaCl_2$, results.

$$BaCO_3 + 2\ HCl = BaCl_2 + H_2O + CO_2$$

It forms crystals having the composition $BaCl_2 \cdot 2\ H_2O$, which lose water when heated. It is used as a source of barium sulphate. It is poisonous.

Barium Oxide and Hydroxide. When barium carbonate is heated to intense white heat, it loses carbon dioxide, a residue of *barium oxide*, BaO (baryta), remaining as a grayish powder, the reaction being reversible.

$$BaCO_3 \rightleftarrows BaO + CO_2$$

When barium carbonate is mixed with carbon (lampblack) or something which will yield carbon, such as tar, the carbon exerts a reducing action, and barium oxide is formed, carbon monoxide, CO, being evolved in the process.

$$BaCO_3 + C = BaO + 2\ CO$$

Barium oxide is usually made by heating barium nitrate.

Barium oxide combines with water, with the evolution of a great deal of heat, sufficient in case the water is sprinkled on the oxide to raise the mass to incandescence, and in any case forming *barium hydroxide*, $Ba(OH)_2$, a white powder, moderately soluble in water, and exhibiting the properties of a strong base, inasmuch as it will neutralize acids, forming barium salts.

$$BaO + H_2O = Ba(OH)_2$$

When the solution is allowed to evaporate, crystals may be obtained having the composition $Ba(OH)_2 \cdot 8\ H_2O$.

When barium oxide, BaO, is heated to redness in a current of dry air, it unites with oxygen, forming a gray mass of *barium dioxide*, BaO_2, which, when strongly heated, decomposes into barium oxide and oxygen. It is used in obtaining oxygen from air.

$$2\ BaO + O_2 = 2\ BaO_2$$

Insoluble Barium Compounds. *The formation of the insoluble salts of barium as precipitates from solutions of the barium salts may be employed to identify barium compounds.* Thus, when a soluble carbonate, like sodium carbonate, Na_2CO_3, is added to a solution of a barium compound, like barium nitrate, $Ba(NO_3)_2$, a white precipitate of *barium carbonate*, $BaCO_3$, very slightly soluble in water, is formed.

$$Ba(NO_3)_2 + Na_2CO_3 = \mathbf{BaCO_3} + 2\ NaNO_3$$

When sulphuric acid, or a soluble sulphate, like potassium sulphate, is added to a solution of barium nitrate, white *barium sulphate*, $BaSO_4$, is precipitated.

$$Ba(NO_3)_2 + H_2SO_4 = \mathbf{BaSO_4} + 2\ HNO_3$$

When to a solution of barium nitrate a soluble chromate, like potassium chromate, K_2CrO_4 (or potassium dichromate, $K_2Cr_2O_7$), is added, a yellow crystalline precipitate of *barium chromate*, $BaCrO_4$, forms. This compound is used in yellow paint.

$$Ba(NO_3)_2 + K_2CrO_4 = \mathbf{BaCrO_4} + 2\ KNO_3$$

Barium. *Barium* is prepared by the electrolysis of fused barium chloride, $BaCl_2$.

$$BaCl_2 = Ba + Cl_2$$

It is a bright yellow metal of specific gravity 3.6, readily oxidizes spontaneously in air, and decomposes water energetically at ordinary temperatures. It is malleable, ductile, and fuses at red heat.

Spectrum. Barium compounds when volatilized impart a pale green color to flame, and emit a complex spectrum containing four characteristic green lines.

Summary. *The common acids act upon the native barium carbonate to form white soluble or insoluble barium salts. Barium carbonate and barium hydroxide may be decomposed by heating with formation of barium oxide, which combines with water to form barium hydroxide. By heating barium oxide to redness in dry air barium dioxide is formed, which at high temperature evolves oxygen. The sparingly soluble barium hydroxide and the insoluble barium sulphate and barium carbonate may be formed as white precipitates. Barium chromate may be formed as a pale yellow precipitate. Barium compounds impart a yellowish green color to flame, and exhibit a spectrum containing four green lines.*

RADIUM, Ra, 225

Radium, first recognized as an element by M. and Mme. Curié, is unknown in free condition. Compounds of radium, exhibiting characteristic spectra, and in general resembling the corresponding compounds of barium, have been prepared, but lack of material has thus far prevented the full study of their chemical relations. Radium occurs in several minerals bearing the element uranium, and at present is obtained from the residues left after extracting uranium from the mineral *uraninite* or *pitchblende*. A ton of such residue yields 10 to 15 kilograms of barium chloride or barium bromide, with which is associated the corresponding radium salt to the extent of 0.2 to 0.3 grams, and the radium salt, being the more insoluble, is separable from the barium salt by fractional crystallization.

Known compounds of radium are: *radium chloride*, $RaCl_2$; *radium bromide*, $RaBr_2$, easily hydrolyzed in ordinary air; and *radium nitrate*, $Ra(NO_3)_2$, and *radium hydroxide*, $Ra(OH)_2$, easily converted to insoluble *radium carbonate*, $RaCO_3$.

Radium compounds are characterized by the possession of *radio-activity*, or the capacity to emit Becquerel rays which, though incapable of being reflected, refracted, or polarized, act upon the photographic plate, render gases through which they pass conductors of electricity, and penetrate black paper and metals. The radio-activity of radium salts increases from the beginning of the process of crystallization and drying to a maximum, which remains constant so long as the salt is left to itself. Salts of radium are luminous and continually emit heat, and peculiar rays causing other substances to become phosphorescent, giving to dielectrics, like petroleum and carbon disulphide, some slight electrical conductivity, exerting certain physiological effects like the destruction of germs and living tissues, and manifesting ability to impart similar radio-active properties to neighboring substances. When a salt of radium, solid or in solution, is placed in a vessel containing air, the interior walls of the vessel become radio-active, and any solid substance put within the vessel likewise becomes radio-active. Furthermore, substances within a second vessel communicating with the first only by a capillary tube acquire radio-activity after a sufficient time. So it appears that radium compounds emit a radio-active emanation, and experiment shows this to be condensible at −150°, and convertible into other products, one of which proves to be the element helium.

Much study has been put upon the properties of the rays emitted by radium, but the discussion of these matters, though of great interest, would lead too far. It appears to be the case that radio-activity is a property possessed in greater or less degree by many forms of matter, and the phenomena suggest the possibility of disintegration of some chemical elements.

CHAPTER VI

PRIMARY SERIES—GROUP III

Boron, B, 11
Aluminium, Al, 27.1
SCANDIUM, Sc, 44.1
YTTRIUM, Yt, 89.0
LANTHANUM, La, 138.9

Group III.

THE elements of Group III of the primary series do not occur free in the earth. Aluminium, which occurs in great abundance in many rocks, and in all clay soils, is a common commercial product; boron, occurring in a few minerals, and in compounds dissolved in waters of volcanic regions, and yttrium and lanthanum, constituents of certain rare minerals, have been prepared only in small quantities in the laboratory, while scandium is not known in free condition.

Boron.

Boron is known as a black powder, and sometimes as more or less colored transparent crystals which, however, are not quite pure boron. The amorphous powdery boron oxidizes when heated, and at red heat decomposes water, forming a normal hydroxide, $B(OH)_3$, which may be decomposed into various oxy-hydroxides, and into an infusible oxide. The boron hydroxides act usually as weak acids; and boron oxide, when fused with certain basic hydroxides, or oxides, or with some salts of positive elements, forms salts in which boron is a part of a negative ion. Boron hydroxide, $B(OH)_3$, boric acid, and some salts of which sodium tetraborate, $Na_2B_4O_7$, *borax*, is the most important, corresponding to various oxy-hydroxides of boron, are the commonly occurring native compounds of boron. In the distinctly acidic nature of its hydroxides boron differs from any of the elements of the preceding groups.

Borax.

Aluminium is a white lustrous metal of low specific gravity, oxidizing when strongly heated, attacked by acids, and conducting electricity.

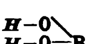
Aluminium. Its oxide is extremely insoluble and infusible. The normal hydroxide, $Al(OH)_3$, which may be formed by indirect methods, exhibits the properties of a weak base, neutralizing the common acids with the formation of salts in which aluminium is a positive ion; but both it and the oxyhydroxide, $AlO(OH)$, produced by heating the normal hydroxide, are capable of neutralizing strong bases with the formation of *aluminates*, salts in which aluminium is a constituent of a negative ion. In nature we find aluminium in the oxide *corundum*, Al_2O_3; in the hydroxides *gibbsite*, $Al(OH)_3$, *diaspore*, $AlO(OH)$, and *bauxite*, $Al_2O(OH)_4$, containing more or less iron oxide; in many complex silicates, such as the *feldspars* (*orthoclase*, $KAlSi_3O_8$) and the *clays* (*kaolinite*, $Al_2H_4Si_2O_9$); and as *cryolite*, $AlF_3 \cdot 3NaF$, a double fluoride, and in *aluminates*, such as *spinel*, $Mg(AlO_2)_2$, *chrysoberyl*, $Gl(AlO_2)_2$, and *gahnite*, $Zn(AlO_2)_2$.

Rare Earths. Scandium, yttrium, lanthanum, like certain similar elements of succeeding groups, are known as *rare earth elements*, because they are found only in small amounts in a few rare earthy minerals. The oxides of these elements, like the oxides of calcium and other elements in the preceding group, glow brightly when heated. Scandium is of especial interest because its existence was suggested in 1863 by Mendeléeff, who, from considerations based upon the periodic law, predicted its atomic weight, and the properties of some of its compounds, ten years before the oxide was discovered.

The elements of the third group of the primary series show generally in their compounds a valence of III.

Boron, B, 11

Boric Acid. We may commence our study of boron with the naturally occurring *boric acid*, H_3BO_3 (boron hydroxide), known as brilliant, colorless, crystalline scales, which are moderately soluble in cold water but are much more soluble in hot water. When its solution is boiled, some of the boric acid volatilizes with the steam, from which it may be obtained in crystallized form by condensation and concentration of the resulting solution. In some volcanic regions, especially in Tuscany, steam charged with boric acid issues from the earth and condenses in pools. By slowly evaporating the waters of such pools crystallized boric acid may be obtained. Sometimes artificial pools are constructed by building walled basins over the volcanic vents or *fumaroles*, and allowing the steam jets or *soffioni* to bubble through water contained in them, the resulting solution, which may contain as much as 2 per cent. of boric acid, being concentrated by the natural heat. In many places artificial fumaroles have been made by boring. Boric acid is also produced from *tincal*, $Na_2B_4O_7 \cdot 10\,H_2O$ (borax), and it occurs in crystallized form as the mineral *sassolite*. It is used as an antiseptic in medicine and surgery, and as a preservative for meat.



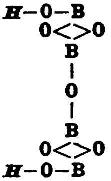
When the normal boron hydroxide, orthoboric acid, H_3BO_3, is heated to 100°, an ideal molecule loses a molecule of water, forming an oxyacid known ordinarily as *metaboric acid*, HBO_2, a volatile white powder.

$$H_3BO_3 = HBO_2 + H_2O$$

$H-O-B=O$

When the metaboric acid, HBO_2, is heated at 140°, one molecule of water is removed from four molecules of the acid, forming another oxyacid known as *tetraboric acid*, $H_2B_4O_7$, which contains four atoms of boron in each molecule.

$$4\,HBO_2 = H_2B_4O_7 + H_2O$$

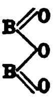


When the tetraboric acid, $H_2B_4O_7$, is heated strongly at red heat, the remaining molecule of water is removed from the molecule of the acid, leaving a fused residue of *boron trioxide*, slightly volatile at high heat, for which the simplest symbol is B_2O_3.

$$H_2B_4O_7 = 2\,B_2O_3 + H_2O$$

Boron trioxide may be formed directly by heating orthoboric acid, H_3BO_3, to redness.

$$2\,H_3BO_3 = B_2O_3 + 3\,H_2O$$



Boron trioxide, B_2O_3, is a brittle glassy substance, very hygroscopic, combining readily with water with the formation of orthoboric acid. It is volatile only at a very high temperature, and consequently, when fused with hydroxides or salts of other elements which it can decompose with the liberation of an easily volatile product, it forms with the oxides of the positive elements of such compounds salts corresponding to boric acid, metaboric acid, or tetraboric acid, according to the proportions in which the interacting substances are taken.

Sodium Borates. *We recognize boron trioxide, made by heating the boric acids, as an acidic oxide, and we may use it as a starting point for the formation of the salts of the boric acids, — the orthoborates, metaborates, and tetraborates respectively, — in which boron is a constituent of the negative ion.*

By fusing boron trioxide, B_2O_3, with sodium hydroxide, in such proportions that six gram-equivalents of the hydroxide will act on each gram-equivalent of the oxide, a hard crystalline mass of *sodium orthoborate*, Na_3BO_3, may be formed.

$$6\,NaOH + B_2O_3 = 2\,Na_3BO_3 + 3\,H_2O$$

The same compound may be obtained by fusing together boron trioxide and sodium carbonate, in the proportion of three gram-equivalents of the carbonate to each gram-equivalent of the oxide.

$$3\,Na_2CO_3 + B_2O_3 = 2\,Na_3BO_3 + 3\,CO_2$$

Sodium orthoborate dissolves in water with hydrolytic formation of *sodium metaborate*, $NaBO_2$, and sodium hydroxide, simultaneously.

$$Na_3BO_3 + H_2O = NaBO_2 + 2\,NaOH$$

When boron trioxide and sodium hydroxide are fused together in such proportions that each gram-equivalent of the oxide will interact with two gram-equivalents of the hydroxide, *sodium metaborate*, $NaBO_2$, is formed as a crystalline mass,

$$2\,NaOH + B_2O_3 = 2\,NaBO_2 + H_2O$$

and the same compound may be obtained by fusing together boron trioxide and sodium carbonate in required proportions.

$$Na_2CO_3 + B_2O_3 = 2\,NaBO_2 + CO_2$$

Sodium metaborate is soluble in water and may be recovered from its solution as crystals containing water of crystallization and having the composition $NaBO_2 \cdot 2\,H_2O$.

Sodium tetraborate, $Na_2B_4O_7$ (borax), may be obtained by fusing boron trioxide with sodium hydroxide in such proportions that equal numbers of gram-equivalents of the two substances will act upon one another.

$$2\,NaOH + 2\,B_2O_3 = Na_2B_4O_7 + H_2O$$

The same compound may be got by similarly fusing **boron trioxide** with a suitable amount of sodium carbonate.

$$Na_2CO_3 + 2\ B_2O_3 = Na_2B_4O_7 + CO_2$$

Sodium tetraborate dissolves in water and may be crystallized therefrom either with five molecules of water of crystallization, $Na_2B_4O_7 \cdot 5\ H_2O$, or, as is the case with ordinary borax, with ten molecules of water, $Na_2B_4O_7 \cdot 10\ H_2O$. When crystallized borax is heated it increases largely in volume, loses water, and at 880° forms an anhydrous transparent glassy mass, $Na_2B_4O_7$. Anhydrous borax has the property of combining with many oxides of metals when fused with them, forming transparent glassy beads of colors which are often characteristic of the oxides employed, and for this reason borax is useful as a flux, in welding metals, and in glazing and enameling metals and pottery. It is employed in soap-making and in dyeing, and is also used as a preservative for meat, and in medicine. Borax occurs native as the mineral *tincal*. In commerce it is prepared by purifying the natural product, and by acting upon orthoboric acid with sodium carbonate in solution or in fusion.

We have seen that when boron trioxide is fused with the maximum amount of sodium hydroxide with which it can act, sodium orthoborate is formed, and that when less than the maximum amount of sodium hydroxide is employed, sodium metaborate or sodium tetraborate may result. Similarly from a borate containing a smaller proportion of sodium may be obtained a borate containing a larger proportion of sodium by fusion with sodium hydroxide or sodium carbonate.

Sodium metaborate may be formed by fusing sodium tetraborate with the proper amount of sodium hydroxide, and sodium orthoborate may be obtained by fusing sodium metaborate with the requisite quantity of sodium hydroxide. Thus, when sodium tetraborate, $Na_2B_4O_7$, is fused with sodium hydroxide in the proportion of one gram-equivalent of the former to two gram-equivalents of the latter, *sodium metaborate*, $NaBO_2$, is produced,

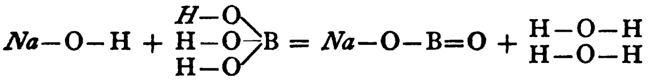
$$2\ NaOH + Na_2B_4O_7 = 4\ NaBO_2 + H_2O$$

and when sodium metaborate, $NaBO_2$, is fused with sodium hydroxide, in the proportion of one gram-equivalent of the former to two gram-equivalents of the latter, *sodium orthoborate*, Na_3BO_3, is the product.

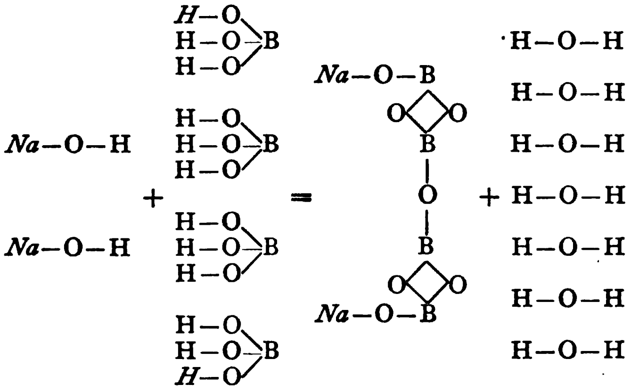
$$2\ NaOH + NaBO_2 = Na_3BO_3 + H_2O$$

In like manner by fusing sodium tetraborate with the proper amount of sodium carbonate we may get sodium metaborate, while the latter, fused with sodium carbonate in proper amount, will give sodium orthoborate.

Sodium metaborate and sodium tetraborate may likewise be formed in solution by the action of orthoboric acid upon the proper amounts of sodium hydroxide. The formation of sodium orthoborate in this manner, however, takes place, if at all, only in the presence of an excess of sodium hydroxide, since sodium orthoborate is hydrolyzed by pure water. When sodium hydroxide and orthoboric acid act upon one another in proper proportion, sodium metaborate may be crystallized from the solution with two molecules of water, having the composition $NaBO_2 \cdot 2\,H_2O$.



With still other proportions of reacting substances the sodium tetraborate may be formed and crystallized from the solution with ten molecules of water, $Na_2B_4O_7 \cdot 10\,H_2O$.



Similar crystals of sodium tetraborate may be obtained from a solution made by boiling orthoboric acid with sodium carbonate.

$$Na_2CO_3 + 4\,H_3BO_3 = Na_2B_4O_7 + 6\,H_2O + CO_2$$

This is a common commercial method for making borax.

Action of Acids upon Borates. Sodium orthoborate, as we have seen, is hydrolyzed with the formation of sodium metaborate. Sodium metaborate and sodium tetraborate are readily decomposed in water by acids, and from the solutions thus formed salts containing greater proportionate amounts of boron, or, in case the acids are employed in excess, boric acid, may be obtained, the metals in either case forming salts with the acids taken. By acting upon sodium metaborate, $NaBO_2$, in solution in water, with a proper amount of sulphuric acid, sodium tetraborate may be made and crystallized from the solution with ten molecules of water, $Na_2B_4O_7 \cdot 10\,H_2O$, sodium sulphate also being formed.

$$4\,NaBO_2 + H_2SO_4 = Na_2B_4O_7 + H_2O + Na_2SO_4$$

If, however, a sufficient amount of sulphuric acid be added to the solution of sodium metaborate, orthoboric acid, H_3BO_3, may be crystallized from the sufficiently concentrated solution.

$$2\,NaBO_2 + H_2SO_4 + 2\,H_2O = 2\,H_3BO_3 + Na_2SO_4$$

Similarly, orthoboric acid may be got by acting upon sodium tetraborate, $Na_2B_4O_7$, with sufficient sulphuric acid, and evaporating the solution.

$$Na_2B_4O_7 + H_2SO_4 + 5\,H_2O = 4\,H_3BO_3 + Na_2SO_4$$

Even carbon dioxide, CO_2, will decompose sodium metaborate, $NaBO_2$, in solution in water, from which sodium tetraborate, $Na_2B_4O_7 \cdot 10\,H_2O$, may be crystallized.

$$4\,NaBO_2 + CO_2 = Na_2B_4O_7 + Na_2CO_3$$

The action of carbon dioxide on sodium metaborate may go so far as to form some boric acid, though carbon dioxide in water is not able to produce the boric acid to such an extent that it may be crystallized from the solution.

Metaborates and tetraborates of other elements than sodium are also known. Orthoborates are formed only by the fusion together of the proper proportions of boron trioxide and a fusible basic oxide, or hydroxide, or the corresponding carbonate; and such orthoborates are, if soluble, hydrolyzed in water solution. Salts corresponding to some other oxyacids of boron, theoretically derivable by dehydration from several molecules of orthoboric acid, in a manner similar to that in which tetraboric acid is derivable, are also known.

Certain hydroxides of carbon-hydrogen radicals, such as the alcohols, interact with boron trioxide with the formation of orthoborates as well as metaborates. Thus, when an excess of methyl alcohol, CH_3OH, acts upon boron trioxide, *methyl orthoborate*, $(CH_3)_3BO_3$, is formed,

$$6\,CH_3OH + B_2O_3 = 2\,(CH_3)_3BO_3 + 3\,H_2O$$

while in case ethyl alcohol, C_2H_5OH, is employed, *ethyl orthoborate*, $(C_2H_5)_3BO_3$, is formed in like manner. When the boron trioxide, however, is in excess in the presence of methyl alcohol, *methyl metaborate*, CH_3BO_2, is formed,

$$2\,CH_3OH + B_2O_3 = 2\,CH_3BO_2 + H_2O$$

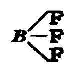
while, if ethyl alcohol be employed, *ethyl metaborate*, $C_2H_5BO_2$, results. These borates of the carbon-hydrogen radicals are colorless liquids, and are readily volatile. They impart to flame a fine green color characteristic of the boron compounds.

Boron Salts.

We also recognize boron trioxide as an oxide of very weak basic properties, since it will act upon a very few acids with the formation of salts in which boron acts as a positive ion. Although no nitrate of boron is known, disulphuric acid, $H_2S_2O_7$, will act upon boron trioxide with the formation of a substance which may be recovered from solution as crystals which are decomposed by water and by heating, with evolution of sulphur trioxide, SO_3, and which have the composition, $B(HSO_4)_3$, corresponding to an acidic sulphate of boron.

When boron trioxide is treated with an excess of concentrated phosphoric acid, H_3PO_4, an amorphous residue may be obtained which is infusible and not attacked by acids, and has the composition BPO_4, showing it to be a neutral phosphate of boron.

Binary Compounds of Boron.



A few binary compounds of boron may be formed in which boron as a positive ion is combined with negative elements.

When gaseous hydrofluoric acid, HF, acts upon boron trioxide, B_2O_3, *boron trifluoride*, BF_3, a strongly fuming colorless gas, is produced.

$$B_2O_3 + 6\,HF = 2\,BF_3 + 3\,H_2O$$

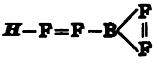
A practical method for its preparation consists in heating together the proper amounts of boron trioxide, B_2O_3, calcium fluoride, CaF_2, and sulphuric acid, in sufficient excess to hold in combination the water set free in the reaction.

$$B_2O_3 + 3\,CaF_2 + 3\,H_2SO_4 = 2\,BF_3 + 3\,H_2O + 3\,CaSO_4$$

Boron fluoride may also be made directly by burning boron in an atmosphere of fluorine gas.

$$2\,B + 3\,F_2 = 2\,BF_3$$

Boron fluoride has a pungent odor. It has a strong attraction for water, dissolving in it readily, and even removing the elements of water from certain carbon compounds to the extent of charring them.



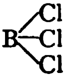
When boron fluoride, BF_3, dissolves in water, partial hydrolysis takes place, and *hydrogen borofluoride*, HBF_4, is formed, along with some orthoboric acid.

$$4\,BF_3 + 3\,H_2O = 3\,HBF_4 + H_3BO_3$$

This compound, known sometimes as "fluoboric acid," which has not been prepared in pure condition, is a monobasic acid, forming salts in which the hydrogen has been replaced by a metal, as, for example, potassium fluoborate, KBF_4. It may be regarded as a peculiar acid, resembling metaboric acid, HBO_2, with two fluorine atoms taking the place of each of the two oxygen atoms of the latter.

Boron ignites spontaneously when brought in contact with chlorine with the formation of *boron trichloride*, BCl_3, a colorless liquid.

$$2\,B + 3\,Cl-Cl =$$



Boron trichloride is most conveniently prepared by passing a stream of dry chlorine through a porcelain tube containing an ignited mixture of boron trioxide, B_2O_3, and carbon.

$$B_2O_3 + 3\,C + 3\,Cl_2 = 2\,BCl_3 + 3\,CO$$

Boron trichloride is a colorless liquid fuming strongly in air, boiling at 17°, and readily hydrolyzed on contact with water, with the formation of boric acid.

$$BCl_3 + 3\,H_2O = H_3BO_3 + 3\,HCl$$

Boron nitride, BN, a white amorphous powder, is formed when amorphous boron or a mixture of boron trioxide and carbon is heated in nitrogen or ammonia.

Boron carbide, B_6C, black, crystalline, and exceedingly hard, is formed when boron and carbon are heated together in the electric furnace.

Boron hydride, BH_3, is known as a gas, but only in mixture with hydrogen.

Boron. *Boron* exists in free condition in two varieties, — an amorphous black powder, and in impure condition as transparent crystals. Amorphous boron was first obtained by Gay-Lussac by heating boron trioxide with potassium. The element has more recently been prepared by Moissan in very pure amorphous form, of specific gravity 2.43, by fusing boron trioxide with magnesium. Crystalline boron of specific gravity 2.63 was prepared by Wöhler in 1856 by fusing amorphous boron with aluminium, and then cooling the mixture, and removing the aluminium by hydrochloric acid. During the cooling the boron, together with some aluminium, separated in large, transparent crystals which were left as a residue when the aluminium was removed. Boron is unacted upon by air at ordinary temperatures, but when amorphous boron is heated in air it is oxidized. Boron is acted upon by nitric acid, by sulphuric acid, and by alkali carbonates in a state of fusion; and combines directly with many other elements.

Flame Coloration by Boron Compounds.

To identify the presence of a boron compound we may best take advantage of the fact that the volatile compounds of boron impart to flame a fine green color. In the case of a borate, such as sodium tetraborate (borax), we may best carry out the test for the presence of boron by reducing the salt to the condition of a fine powder, placing it in a porcelain dish, moistening with concentrated sulphuric acid, and covering with methyl alcohol or with ethyl alcohol. In this way the volatile methyl borate, or ethyl borate, is formed, and upon igniting the alcohol the green color characteristic of boron will be observed in the margins of the flame which plays over the burning liquid. The color may be intensified by stirring and warming the mixture.

Summary.

By heating native orthoboric acid, metaboric acid, tetraboric acid, and boron trioxide are formed. By fusing boron trioxide with sodium hydroxide or sodium carbonate in suitable proportions, the corresponding orthoborate, metaborate, and tetraborate may be obtained. Sodium orthoborate is readily hydrolyzed in solution. Sodium metaborate may be obtained from sodium tetraborate, and sodium orthoborate may be made from sodium metaborate, by fusion with sodium hydroxide. Sodium metaborate and sodium tetraborate may also be obtained by acting upon sodium hydroxide with boric acid in proper proportions. The borates of the alkali elements are white salts, soluble in water and decomposed by acids. The borates of certain carbon-hydrogen radicals are volatile and impart a characteristic green color to flame.

Boron fluoride, a colorless gas, and boron chloride, a colorless, very volatile liquid, are both made by direct combination of their elements, and *boron fluoride may also be made by the interaction of boron trioxide and hydrofluoric acid; hydrogen borofluoride is made by the hydrolysis of boron fluoride. Other binary compounds of boron and other elements are known. Boron may be prepared by reducing boron trioxide with potassium or magnesium.*

Aluminium, Al, 27.1

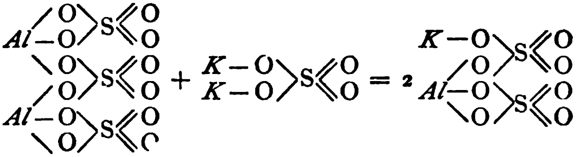
Clays. The most abundant and widely distributed naturally occurring compounds of aluminium are its silicates, or salts of the silicic acids, H_4SiO_4, H_2SiO_3, etc., of which the most important is *kaolinite*, $H_4Al_2Si_2O_9$, white in color, and the purest known form of *clay*. The more common colored forms of clay have a composition similar to that of kaolinite, except that they contain small quantities of iron and other elements. The clays result from the weathering of certain rocks, such as granite, gneiss, syenite, etc., which contain *feldspars* (*orthoclase*, $KAlSi_3O_8$), *mica* (*muscovite*, $H_2KAl_3Si_3O_{12}$), and other complex aluminium silicates. There are still other complex compounds of aluminium, of which the red *garnets*, $(Mg, Fe, Ca)_3Al_2(SiO_4)_3$, etc., the yellow *topaz*, $Al_2F_2SiO_4$, and the green *beryl*, $Gl_6Al_4(SiO_3)_{12} \cdot H_2O$, prized as *precious stones*, are typical. *Ultramarine* (lapis-lazuli), a complex sodium aluminium silicate containing sulphur, is found native in Asia, and is made artificially on a large scale, its splendid blue color rendering it useful for ornamentation. The *turquoise* is an aluminium phosphate colored by copper.

Aluminium Sulphate. When aluminium silicate, $H_4Al_2Si_2O_9$ (*kaolinite*), is heated with a suitable amount of concentrated sulphuric acid, a white gelatinous precipitate is formed, containing metasilicic acid, H_2SiO_3, which, after addition of water, may be removed by filtration, while *aluminium sulphate*, $Al_2(SO_4)_3$, remains in the solution, from which it may be recovered in the form of thin scales of pearly luster, having the composition $Al_2(SO_4)_3 \cdot 18\,H_2O$.

$$H_4Al_2Si_2O_9 + 3\,H_2SO_4 = Al_2(SO_4)_3 + 2\,H_2SiO_3 + 3\,H_2O$$

When heated, the crystallized aluminium sulphate loses its water of crystallization, becoming anhydrous $Al_2(SO_4)_3$. It is usually prepared commercially by treating clay, or *bauxite* (impure $Al_2O(OH)_4$), or pure aluminium hydroxide, $Al(OH)_3$, with sulphuric acid; also by treating *cryolite*, $3\,NaF \cdot AlF_3$, with calcium hydroxide and then with sulphuric acid. It is at the present time largely used in place of alum. Certain basic *aluminium sulphates*, such as *aluminite*, $Al_2(OH)_4SO_4 \cdot 7\,H_2O$, are found native, and may be prepared artificially.

Alums. When to a solution of aluminium sulphate, potassium sulphate is added, the solution upon evaporation yields beautiful large octahedral crystals of *potassium aluminium sulphate*, $KAl(SO_4)_2 \cdot 12\,H_2O$ (potassium alum), soluble in water, and possessing a sweetish astringent taste.



Potassium alum, when placed over sulphuric acid, loses nine molecules of its water of crystallization, becoming $KAl(SO_4)_2\ 3\,H_2O$, and when heated it loses all the water, becoming white anhydrous $KAl(SO_4)_2$, the so-called *burnt alum*. By adding a little potassium carbonate to a hot solution of potassium alum, and recrystallizing, a variety may be obtained in the form of cubes instead of octahedra. Potassium alum occurs naturally in small quantities alone, and in combination in the mineral *alunite*, $KAl_3(OH)_6(SO_4)_2$. It has been known since ancient times, and is prepared commercially from alunite, and from the pure aluminium sulphate. Its property of crystallizing well facilitates its preparation in pure condition. It is of value in many arts, particularly in dyeing.

Similar double compounds of aluminium sulphate with the sulphates of other univalent elements or groups are known as *alums*, since they crystallize in octahedra or cubes with twelve molecules of water, and are otherwise similar to potassium alum, and are *isomorphous*, a crystal of one kind of alum continuing to increase in size without change of form when placed in a solution of an alum of another kind. Some sulphates of the alkali elements and elements other than aluminium are also known as alums, because they are isomorphous with the true alums. Examples of alums are potassium aluminium sulphate (potassium alum), $KAl(SO_4)_2 \cdot 12\,H_2O$, ammonium aluminium sulphate (ammonium alum), $NH_4Al(SO_4)_2 \cdot 12\,H_2O$, and sodium aluminium sulphate (sodium alum), $NaAl(SO_4)_2 \cdot 12\,H_2O$. Other common salts, likewise called alums, are ammonium ferric sulphate (iron alum), $NH_4Fe(SO_4)_2 \cdot 12\,H_2O$, and potassium chromium sulphate (chromium alum), $KCr(SO_4)_2 \cdot 12\,H_2O$.

Aluminium Hydroxide. When to a solution of aluminium sulphate, $Al_2(SO_4)_3$, or of any soluble salt of aluminium, ammonium hydroxide is added, a voluminous white hydrogel of *aluminium hydroxide*, $Al(OH)_3$, very slightly acted upon by an excess of the reagent, is precipitated.

$$Al_2(SO_4)_3 + 6\,NH_4OH = 2\,Al(OH)_3 + 3\,(NH_4)_2SO_4$$

Aluminium hydroxide may also be formed by adding to a solution of aluminium sulphate an alkali hydroxide, such as sodium hydroxide. In such cases, however, care must be taken to add the reagent in the required amount only, since as we shall see later aluminium hydroxide is acted upon by an excess of alkali hydroxides.

$$Al_2(SO_4)_3 + 6\,NaOH = 2\,Al(OH)_3 + 3\,Na_2SO_4$$

When aluminium hydroxide is moderately heated, it loses one molecule of water, forming an aluminium oxyhydroxide, $AlO(OH)$.

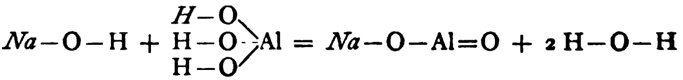
$$Al(OH)_3 = AlO(OH) + H_2O$$

The normal aluminium hydroxide is found native as *gibbsite*, $Al(OH)_3$, while the oxyhydroxides, *diaspore*, $AlO(OH)$, and *bauxite*, $Al_2O(OH)_4$, the latter containing some iron oxide, are also well-known minerals.

Freshly precipitated aluminium hydroxide acts like a weak acid since it will neutralize strong bases with the formation of salts in which aluminium is a constituent of the negative ion; and it also behaves as a weak base, neutralizing acids with the formation of salts in which aluminium is positive.

Aluminates. *Aluminium hydroxide neutralizes strongly basic hydroxides with formation of aluminates — salts in which aluminium is a constituent of the negative ion.*

Thus, when to freshly precipitated aluminium hydroxide, held in suspension, is added a solution of sodium hydroxide, the precipitate disappears, forming a clear solution, from which, by evaporation in a vacuum and treatment of the residue with alcohol, a *sodium aluminate* of the composition $NaAlO_2$, corresponding to metaluminic acid, $HAlO_2$, may be obtained.



$$\mathit{Na}-O-H + \begin{matrix} \mathit{H}-O \\ H-O \\ H-O \end{matrix}\!\!>\!Al = \mathit{Na}-O-Al{=}O + 2\,H-O-H$$

Other aluminates of this type are known, and with weaker bases, like calcium hydroxide, aluminates may be formed corresponding to each of the three aluminium hydroxides, $Al(OH)_3$, $AlO(OH)$, $Al_2O(OH)_4$.

The aluminates are readily decomposed by acids, and even by carbon dioxide, CO_2, with the formation of a very basic carbonate, or, in boiling solution, of aluminium hydroxide.

$$2\,NaAlO_2 + CO_2 + 3\,H_2O = 2\,Al(OH)_3 + Na_2CO_3$$

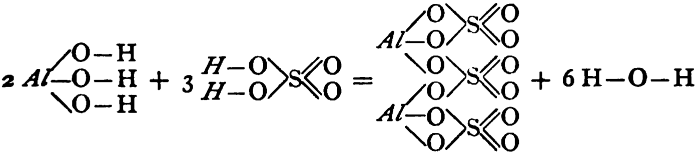
Some aluminates are insoluble in water and may be produced as precipitates by adding suitable salts to solutions of aluminates. Thus, when to a solution of sodium aluminate, $NaAlO_2$, a soluble calcium compound, like calcium chloride, $CaCl_2$, is added, a precipitate of white *calcium aluminate*, $Ca(AlO_2)_2$, is obtained.

$$2\,NaAlO_2 + CaCl_2 = Ca(AlO_2)_2 + 2\,NaCl$$

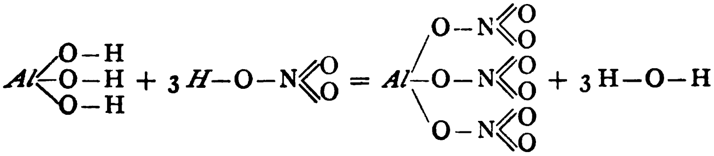
Strontium aluminate, $Sr(AlO_2)_2$, and barium aluminate, $Ba(AlO_2)_2$, are similarly formed. Many aluminates are found native as crystallized minerals, such as *spinel*, $Mg(AlO_2)_2$, *chrysoberyl*, $Gl(AlO_2)_2$, and *gahnite*, $Zn(AlO_2)_2$. When soluble aluminates are acted upon by ammonium chloride, especially in hot solutions, aluminium hydroxide is formed.

$$NaAlO_2 + NH_4Cl + 2\,H_2O = Al(OH)_3 + NaCl + NH_4OH$$

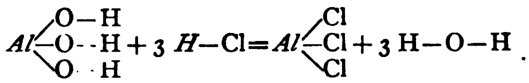
Aluminium Salts. *Aluminium hydroxide may be neutralized by strong acids with formation of salts in which aluminium is the positive ion.* Thus, when sulphuric acid is added to freshly precipitated aluminium hydroxide, held in suspension in water, a clear solution is formed, from which *aluminium sulphate*, $Al_2(SO_4)_3$, may be recovered.



When nitric acid acts upon aluminium hydroxide, *aluminium nitrate*, $Al(NO_3)_3$, is formed in the solution.



When hydrochloric acid acts upon aluminium hydroxide, the resulting solution contains *aluminium chloride*, $AlCl_3$.



$$Al\begin{matrix}-O-H\\-O-H\\-O-H\end{matrix} + 3\,H-Cl = Al\begin{matrix}-Cl\\-Cl\\-Cl\end{matrix} + 3\,H-O-H$$

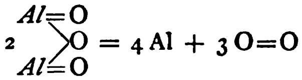
Soluble salts of aluminium in which that element is positive are more or less hydrolyzed by water, their solutions turning litmus red.

Aluminium Oxide. When aluminium hydroxide, freshly precipitated, is heated, it loses water, forming a gum-like, partly dehydrated mass, which when fully dehydrated yields *aluminium oxide*, Al_2O_3 (alumina), a white powder. The oxide may be acted upon by concentrated acids, if it has not been too strongly heated, but after ignition at high temperatures it becomes exceedingly hard and infusible, and is practically unattacked by acids.

$$2\,Al(OH)_3 = Al_2O_3 + 3\,H_2O$$

Aluminium oxide is found native as *corundum;* of which mineral the *ruby* and the *sapphire* are transparent and finely colored varieties. Impure corundum, containing some iron oxide, is used under the name of *emery* for abrasive purposes, and artificial corundum is similarly employed.

Aluminium oxide, Al_2O_3, fused in the electric arc and then acted upon by the electric current, breaks down into *aluminium* and oxygen.



$$2\;\begin{matrix}Al=O\\ \;\;>O\\ Al=O\end{matrix} = 4\,Al + 3\,O=O$$

Aluminium. *Aluminium* was first prepared by Wöhler, in 1827, by the reduction of aluminium chloride, $AlCl_3$, by potassium, and in 1856 it was made commercially by St. Claire-Deville by the reduction of a double chloride of aluminium and sodium, in the presence of cryolite, with sodium; and later the metal was reduced from a fused bath of cryolite and sodium chloride by sodium.

$$NaCl \cdot AlCl_3 + 3\,Na = 4\,NaCl + Al$$

The process of reduction by sodium has now been replaced by the electrolytic methods of Héroult and Hall, which consist essentially in decomposing by a current of low voltage and of quantity high enough to sustain the necessary temperature a bath made by fusing together alumina and cryolite. Under the action of the current, aluminium is separated at the cathode while oxygen is liberated at the anode. The aluminium and oxygen thus removed from the bath are replaced by the addition of alumina from time to time, thus making the process continuous.

Aluminium is a white lustrous metal, very ductile and malleable. It is very slightly affected by air at ordinary temperatures, and it oxidizes only with difficulty when strongly heated. It is practically without action upon water at any temperature. It conducts electricity readily. It is the lightest of the useful metals, its specific gravity being 2.58. It melts when heated at 660°, but is not vaporized. On account of its permanency and beautiful luster aluminium is sometimes employed for making vessels and ornamental objects, and its alloys with other elements are very useful. *Aluminium bronze*, consisting of copper with from 5 to 12 per cent. of aluminium, has the color and luster of burnished gold, and is valuable because of its hardness and durability, and its property of not shrinking in the process of casting.

Aluminium in the form of powder has recently found new use as a reducer of metals from their oxides, the heat of formation of aluminium oxide being so high that the reaction between aluminium and many oxides when once started by heat is kept up spontaneously, while the aluminium oxide produced is melted to a mass which crystallizes on cooling. The heat of reaction between aluminium and ferric oxide has found useful application in the Goldschmidt process for welding iron and steel.

Aluminium is acted upon by strong bases with the formation of aluminates of the positive elements of the bases, and the evolution of hydrogen. When aluminium is warmed with sodium hydroxide in solution, *sodium aluminate*, $NaAlO_2$, is formed, and hydrogen is evolved.

$$2\,Al + 2\,NaOH + 2\,H_2O = 2\,NaAlO_2 + 3\,H_2$$

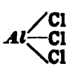
Aluminium is acted upon by common acids, with the exception of nitric acid, with evolution of hydrogen and the formation of salts in which aluminium is the positive ion. When aluminium is acted upon by diluted sulphuric acid, hydrogen is slowly evolved, and *aluminium sulphate*, $Al_2(SO_4)_3$, remains in solution.

$$2\,Al + 3\,H_2SO_4 = Al_2(SO_4)_3 + 3\,H_2$$

When aluminium is attacked by hydrochloric acid, hydrogen is liberated and *aluminium chloride*, $AlCl_3$, is formed in solution.

$$2\,Al + 6\,HCl = 2\,AlCl_3 + 3\,H_2$$

Nitric acid acts slowly and superficially upon aluminium, coating the surface with a thin film of aluminium oxide. The carbon acids, such as acetic acid, $H(C_2H_3O_2)$, act upon pure aluminium only slightly.



Aluminium chloride, $AlCl_3$, which, as we have seen, is readily made in solution by acting upon aluminium hydroxide or upon aluminium with hydrochloric acid, may also be formed in anhydrous condition by the direct union of its constituent elements. Thus, when aluminium is heated in a stream of chlorine, the aluminium chloride is formed as a white mass, which, after sublimation, condenses as white hexagonal leaflets.

$$2\,Al + 3\,Cl_2 = 2\,AlCl_3$$

Aluminium chloride may also be formed by heating in a stream of chlorine a mixture of aluminium oxide and carbon.

$$Al_2O_3 + 3\,C + 3\,Cl_2 = 2\,Al + 2\,AlCl_3 + 3\,CO$$

Aluminium chloride fuses only at high pressure and at a temperature of 193°–194°. At ordinary pressure it boils at 183° before fusing. It is hygroscopic and deliquescent. It may be crystallized with six molecules of water, $AlCl_3 \cdot 6\,H_2O$, by saturating the water solution with hydrochloric acid. When its solution in water is evaporated, it decomposes hydrolytically with the formation of a basic aluminium chloride, which, upon further heating, yields aluminium oxide, Al_2O_3, and hydrochloric acid.

$$2\,AlCl_3 + 3\,H_2O = Al_2O_3 + 6\,HCl$$

It forms many double chlorides and other double salts, such as $AlCl_3 \cdot NaCl$, $AlCl_3 \cdot PCl_5$, $AlCl_3 \cdot POCl_3$. With ammonia gas it forms a yellow powder having the composition $AlCl_3 \cdot 3\,NH_3$. Aluminium chloride is useful in the laboratory as a catalyzer in synthesizing organic compounds.

The determinations of the vapor density of aluminium chloride have thrown important light upon its molecular weight and constitution. In 1857, Deville and Troost found that its vapor density at 440° corresponds to the symbol Al_2Cl_6, a result confirmed later by Friedel and Crafts, who determined the vapor density at from 218° to 440°. In

1887, however, Nilson and Peterson found that at high temperatures above 760° the specific gravity of aluminium chloride corresponds to the symbol $AlCl_3$. In solutions in inert media the symbol of aluminium chloride seems to be Al_2Cl_6, while in solution in active media, like water, the molecule corresponds to the symbol $AlCl_3$.

Summary. *From the native aluminium silicate, by action of sulphuric acid, white soluble aluminium sulphate may be formed. Double sulphates of aluminium and other elements, known as alums, white and soluble in water, may also be formed. From aluminium sulphate solution white gelatinous aluminium hydroxide may be precipitated. Aluminium hydroxide will interact with alkali hydroxides to form soluble aluminates and with common acids to form soluble aluminium salts. Aluminium hydroxide may be decomposed by heating, with formation of aluminium oxyhydroxides and finally of insoluble aluminium oxide. By the reduction of aluminium oxide with carbon, or by electrolytic methods, aluminium may be obtained. Aluminium reacts with acids to form aluminium salts, and combines with chlorine to form soluble aluminium chloride, hydrolyzed in solution by heating.*

SCANDIUM, Sc, 44.1

Scandium is not known uncombined, but scandium oxide and derived salts were prepared in 1879 by Nilson from the minerals *gadolinite* and *euxenite*, in the course of repeated cycles of operations involving the formation and partial decomposition by heat of nitrates and the extraction of residues by boiling water. *Scandium oxide*, Sc_2O_3, is white and infusible, and from it may be prepared compounds in which scandium is a trivalent positive ion. Such are *scandium nitrate*, $Sc(NO_3)_3$, *scandium sulphate*, $Sc_2(SO_4)_3$, *scandium potassium sulphate*, $Sc_2(SO_4)_3 \cdot 3\ K_2SO_4$, *scandium chloride*, $ScCl_3$, known in solution, and *scandium hydroxide*, $Sc(OH)_3$, white and gelatinous, precipitated by alkali hydroxides from solutions of scandium salts and insoluble in excess of the precipitant. The spark spectrum of scandium chloride is characteristic.

YTTRIUM, Yt, 89.0

Yttrium oxide was discovered as a constituent of the mineral *gadolinite* by Mosander in 1843. By suitable fractional treatment of salts prepared from the oxides of gadolinite, yttrium compounds may be isolated. For this purpose fractional precipitation of solutions by potassium chromate, or fractional solution by ammonium carbonate, of the precipitated hydroxides, followed by fractional precipitation of the solutions by acetic acid, are effective methods. The yttrium hydroxide, possibly $Yt(OH)_3$, resulting from the latter procedure or precipitated by ammonium hydroxide from any suitable solution of an yttrium salt, or yttrium oxide, Yt_2O_3, may serve for the preparation of salts in which yttrium appears as a trivalent positive ion.

Yttrium oxide, Yt_2O_3, white and infusible, is obtained by ignition of the hydroxide; *yttrium chloride*, $YtCl_3$, may be obtained by ignition of the oxide with carbon in an atmosphere of chlorine; the hydrated *yttrium chloride*, $YtCl_3 \cdot 6\ H_2O$, may be obtained by the action of hydrochloric acid upon the oxide; *yttrium nitrate*, $Yt(NO_3)_3 \cdot 6\ H_2O$, is crystalline and deliquescent; *yttrium sulphate*, $Yt_2(SO_4)_3 \cdot 8\ H_2O$, and *yttrium potassium sulphate*, $Yt_2(SO_4)_3 \cdot 3\ K_2SO_4$, are also known.

Yttrium is obtained in free condition by electrolysis of anhydrous yttrium chloride, $YtCl_3$, as a gray powder capable of decomposing water, slowly in the cold and more rapidly when hot. The solution of yttrium chloride gives a brilliant and complex spark spectrum.

LANTHANUM, La, 138.9

Lanthanum oxide, La_2O_3, was isolated by Mosander in 1839 from the constituent oxides of the mineral *cerite*, and from it may be prepared the anhydrous *lanthanum chloride*, $LaCl_3$. *Lanthanum*, lustrous and white, oxidizable and combustible in air, of specific gravity 6.16, may be obtained by the electrolysis of the fused chloride; *lanthanum oxide*, La_2O_3, obtained by ignition of the metal, of the hydroxide, or of salts decomposable by heat, is white, and is attacked by water with formation of the hydroxide; *lanthanum hydroxide*, $La(OH)_3$, slightly soluble in water, is easily attacked by acids, even by carbonic acid, forming salts; crystalline hydrated *lanthanum chloride*, $LaCl_3 \cdot 7\ H_2O$, is obtained by evaporating over sulphuric acid the solution of the hydroxide in hydrochloric acid, and upon heating in an atmosphere of hydrogen chloride forms the fusible anhydrous *lanthanum chloride*, $LaCl_3$; *lanthanum nitrate*, $La(NO_3)_3 \cdot 6\ H_2O$, *lanthanum sulphate*, $La_2(SO_4)_3 \cdot 9\ H_2O$, and *lanthanum potassium sulphate*, $La_2(SO_4)_3 \cdot 3\ K_2SO_4$, are easily prepared. Salts of lanthanum show no absorption spectra, but the chloride gives a brilliant and complex spark spectrum.

CHAPTER VII

PRIMARY SERIES—GROUP IV

Carbon, C, 12.00
Silicon, Si, 28.4
TITANIUM, Ti, 48.1
ZIRCONIUM, Zr, 90.6
CERIUM, Ce, 140.25
THORIUM, Th, 232.5

Group IV.

OF the elements of the fourth group of the primary series only carbon is found in free condition. All are found in combination, carbon and silicon compounds being widely distributed in the solid crust of the earth, while the compounds of titanium, zirconium, cerium, and thorium are found in small amounts in a few rare minerals. The elements of the group all may be prepared from their compounds, carbon, silicon, titanium, and zirconium existing in allotropic modifications. All the elements of the group are more or less easily oxidized when heated in air or oxygen. In their chemical properties, carbon and silicon stand apart from the other elements of the group in that they are more electro-negative, their hydroxides like boron hydroxide being distinctively acidic, neutralizing bases to form salts, the *carbonates* and *silicates*, in which carbon and silicon are constituents of negative ions. On the other hand, the hydroxides and oxides of titanium and zirconium act both as acids and as bases, and the hydroxides and oxides of cerium and thorium, like those of the more electro-positive elements, are basic only.

Allotropic Forms of Carbon.

Carbon occurs in three forms, — the transparent colorless *diamond* and the black *graphite*, which are found native, and the common black *amorphous carbon* (soot, charcoal), produced by decomposing animal or vegetable substances by heating out of contact with air. All these forms of carbon are attacked only by

Carbon Compounds. acids which effect oxidation. When carbon is heated in an abundance of air it forms *carbon dioxide*, CO_2, which is found naturally everywhere in the world as a constituent of atmospheric air. The principal carbon compounds found in the earth's crust are the *carbonates*, chiefly *limestone* or impure calcium carbonate, and the hydrocarbons, consisting of hydrogen and carbon, and occurring in *natural gas*, *petroleum*, *coal* and other fossilized vegetable remains. All vegetable and animal matters contain carbon compounds. The solution of carbon dioxide, CO_2, in water, known as the unstable *carbonic acid*, H_2CO_3, interacts with most bases to form carbonates, salts in which carbon is a constituent of the negative ion. In certain binary carbon compounds, like carbon tetrachloride, CCl_4, and carbon disulphide, CS_2, carbon is the positive ion.

Silica and Silicates. Silicon does not occur uncombined in nature; when prepared it is seen as a brown amorphous powder, or as grayish black lustrous crystals, unattacked by ordinary acids, acted upon by hydrofluoric acid. Next to oxygen, silicon is the most abundant element known in combination, since it is the principal constituent of *quartz*, SiO_2, *feldspar*, (*orthoclase*, $KAlSi_3O_8$, *albite*, $NaAlSi_3O_8$, *anorthite*, $CaAl_2Si_2O_8$), *mica* (*muscovite*, $H_2KAl_3Si_3O_{12}$), and the many other minerals which compose the common rocks of the earth's crust. The greater number of the minerals containing silicon are silicates, salts of the unstable *orthosilicic acid*, H_4SiO_4, and its derivates, in which silicon is in the negative ion. In silicon fluoride and silicon chloride, and other binary compounds, silicon is the positive ion.

Rare Earths. Titanium, zirconium, cerium, and thorium, like the rare elements of the preceding group, are known as *rare earth elements*, since they are found only in small quantities in a few rare earthy minerals, such as *rutile*, TiO_2, *zircon*, $ZrSiO_4$, and the complex *cerite* and *thorite*. The oxides of these elements possess the property of glowing brightly when heated, which, in the case particularly of thorium oxide, is turned to account for lighting purposes in gas burners of the *Welsbach* type. The hydroxides of titanium, zirconium, cerium, and thorium, all insoluble substances, act as weak bases, forming salts with the strong acids, while titanium and zirconium act also as weak acids, forming salts with strong bases.

All of the elements of the second group of the primary series form compounds by direct combination with other elements.

In most compounds the elements of the group have an indicated valence of IV, although the utilized valence is frequently less.

Carbon, C, 12.00

Carbon and its Compounds. Carbon is known in three allotropic forms, — the hard transparent and very refractive *diamond*, the soft black *graphite*, and the black *amorphous carbon*, of which the commonest form is ordinary charcoal. All three forms of carbon are solid at all ordinary temperatures, volatile only at the extremely high temperatures of the electric arc, unaffected by solvents, and oxidized when heated suitably in air or oxygen. In other respects, however, the three modifications show important differences, as we shall see when we study them individually. In combination, carbon occurs naturally in *carbohydrates*, containing carbon, hydrogen, and oxygen, including cellulose, starch, and the sugars, and in the *proteids*, containing carbon, hydrogen, oxygen, and nitrogen, and in similar compounds containing these and other elements, and found like the carbohydrates and proteids in vegetable and animal bodies; in *hydrocarbons*, containing carbon and hydrogen, and forming the principal constituent of coal, petroleum, natural gas, and other mineral products produced from vegetable matter by geological agencies; in *carbon dioxide*, CO_2, present in small and variable amounts in the atmosphere; and in the *carbonates*, principally calcium carbonate, $CaCO_3$, and magnesium carbonate, $MgCO_3$, present in large areas of the earth's solid crust.

Diamond. *Diamond* is a transparent, crystalline, and highly refractive mineral. It is the hardest known substance. It is ordinarily colorless, although sometimes it is slightly tinted by the presence of impurities. It has a specific gravity of 3.5. When heated strongly in air or oxygen it becomes completely oxidized. At extremely high temperatures, such as those which may be produced between the terminals of an electric arc, it becomes soft and is transformed into graphite. It is unattacked by ordinary reagents. Since ancient times the diamond has been prized for its great beauty, which is enhanced by cutting and polishing its natural surface, giving it many facets which permit it to disperse the light in all directions. The unit of weight employed in estimating the value of diamonds is the "diamond caret," which is equal to

0.2054 grams. At present most of the diamonds of the world are found in the alluvial soils, as in the Kimberley region in South Africa.

Diamond has been prepared artificially by Moissan, who obtained it by dissolving carbon in molten iron, and suddenly cooling the mixture, when the most of the carbon separated as graphite, while some of the carbon, under the great pressure caused by the expansion of the interior of the mass as it cooled against the already cooled and rigid outer shell, formed small diamond crystals.

Graphite. *Graphite* is found widely distributed in granular condition in granite and other igneous rocks. It is sometimes found as an amorphous grayish black lustrous mass, and occasionally it occurs in hexagonal crystals. It has a specific gravity of 2.25. It readily conducts heat and electricity. When heated in an atmosphere of oxygen it burns with great difficulty. It is soft and is used to lubricate machinery. It makes a dark gray or black streak when rubbed on light colored surfaces, and it is therefore employed in the manufacture of lead pencils. It was once supposed to contain lead, and was therefore called "plumbago" or "black lead." It is mined in Siberia and in California. It may be made artificially by heating carbides of the metals, or coke with intermixed oxides of the metals, in the electric furnace. Graphite thus made is largely employed for electrodes.

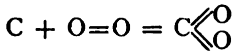
Amorphous Carbon. *Amorphous carbon* may be produced by heating vegetable or animal substances, or products derived from these, out of free contact with the air, the nature of the amorphous carbon produced depending upon the materials selected for heating. Thus, when certain oils, such as turpentine, $C_{10}H_{16}$, a hydrocarbon derived from resinous material and rich in carbon, are burned, the resulting flame is smoky, depositing on adjacent objects a thick coating of *soot* (lampblack) which is largely soft amorphous carbon. A similar deposit may be obtained when common *coal oil* (kerosene), less rich in carbon than turpentine, is allowed to burn in a supply of air insufficient to effect its complete oxidation. Lampblack is an ingredient of printer's ink and of some paints, and is used in calico printing.

Coal. When *coal*, a fossil mineral consisting of a mixture of many different hydrocarbons, and containing from 50 to 98 per cent. of pure carbon, together with some hydrogen, oxygen, nitrogen, and sulphur, is submitted to *dry distillation*, *e.g.* is heated to redness in especially constructed retorts out of contact with air, the hydrocarbons are volatilized, and a grayish or black porous residue, known as *coke*, is obtained. Coke, like coal, is largely employed as a fuel. It ignites at a higher temperature than coal, and burns without evolving smoke. In the back part of the retort in which the coal is distilled the high temperature sometimes causes the decomposition of a portion of the gaseous hydrocarbons which are evolved, forming on the walls of the retort a gray or black deposit of amorphous carbon in compact condition (gas carbon), which has a specific gravity of 2.3, readily conducts electricity, and is largely employed in the manufacture of electrodes and battery plates.

Charcoal. All vegetable and animal bodies contain carbon as an essential constituent. When woody fiber, which consists principally of *cellulose*, $(C_{12}H_{20}O_{10})_n$, a carbohydrate, is subjected to dry distillation, it is decomposed, setting free gaseous hydrocarbons, and leaving a residue of *wood charcoal*, which is a black porous substance, tasteless and odorless, having a specific gravity of 1.57. Wood charcoal is manufactured by heating wood at carefully regulated temperatures in covered heaps known as *charcoal kilns*, or in closed iron retorts. It is readily combustible, and when pure burns without flame or smoke. It is largely used as a fuel. It is employed in metallurgical operations as a reducing agent. When animal tissues, which differ from the woody material principally in the fact that they contain considerable quantities of nitrogen, are subjected to dry distillation, they are partially oxidized, and a residue of black *animal charcoal*, consisting of carbon, together with some nitrogen compounds, is formed. By heating bones in a closed retort and treating the earthy constituents of the bones with acid, a variety of animal charcoal known as *bone black* is obtained. Both wood charcoal and animal charcoal, on account of their extreme porosity, are useful as filters for liquids and possess the property of absorbing gases with great readiness.

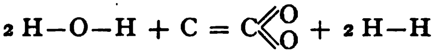
Carbon Oxides. *The compounds of carbon with oxygen are two in number, — carbon dioxide and carbon monoxide.*

Carbon Dioxide. *Carbon dioxide may be made by completely oxidizing carbon, either directly by burning it in an excess of air or oxygen, or by heating it with a suitable oxide.* When the common amorphous carbon (charcoal or coke) burns in an excess of air or oxygen, *carbon dioxide*, CO_2, is formed.



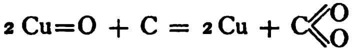
$$\mathrm{C} + \mathrm{O{=}O} = \mathrm{C}\begin{smallmatrix}/\!/\mathrm{O}\\ \backslash\!\backslash\mathrm{O}\end{smallmatrix}$$

The same compound may be formed when a current of steam is passed through a mass of charcoal or coke, heated to incandescence,



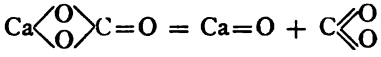
$$2\,\mathrm{H{-}O{-}H} + \mathrm{C} = \mathrm{C}\begin{smallmatrix}/\!/\mathrm{O}\\ \backslash\!\backslash\mathrm{O}\end{smallmatrix} + 2\,\mathrm{H{-}H}$$

and when an intimate mixture of an oxide of a metal, such as copper oxide, CuO, and carbon, is heated to redness.



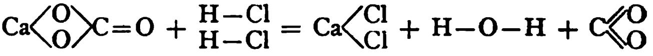
$$2\,\mathrm{Cu{=}O} + \mathrm{C} = 2\,\mathrm{Cu} + \mathrm{C}\begin{smallmatrix}/\!/\mathrm{O}\\ \backslash\!\backslash\mathrm{O}\end{smallmatrix}$$

Carbon dioxide may be set free from some compounds, which contain carbon and oxygen. When a carbonate, such as calcium carbonate, $CaCO_3$ (limestone, marble), is ignited at red heat, *carbon dioxide* is evolved,



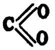
$$\mathrm{Ca}\begin{smallmatrix}/\mathrm{O}\backslash\\ \backslash\mathrm{O}/\end{smallmatrix}\mathrm{C{=}O} = \mathrm{Ca{=}O} + \mathrm{C}\begin{smallmatrix}/\!/\mathrm{O}\\ \backslash\!\backslash\mathrm{O}\end{smallmatrix}$$

and the gas is also liberated when a carbonate is acted upon by an acid such as hydrochloric acid.



$$\mathrm{Ca}\begin{smallmatrix}/\mathrm{O}\backslash\\ \backslash\mathrm{O}/\end{smallmatrix}\mathrm{C{=}O} + \begin{smallmatrix}\mathrm{H{-}Cl}\\ \mathrm{H{-}Cl}\end{smallmatrix} = \mathrm{Ca}\begin{smallmatrix}/\mathrm{Cl}\\ \backslash\mathrm{Cl}\end{smallmatrix} + \mathrm{H{-}O{-}H} + \mathrm{C}\begin{smallmatrix}/\!/\mathrm{O}\\ \backslash\!\backslash\mathrm{O}\end{smallmatrix}$$

Both of these methods are employed for the manufacture of carbon dioxide for commercial purposes. For the uses of the laboratory, carbon dioxide is prepared by acting upon broken bits of marble, contained in a Kipp generator, with hydrochloric acid.



$$\mathrm{C}\begin{smallmatrix}/\!/\mathrm{O}\\ \backslash\!\backslash\mathrm{O}\end{smallmatrix}$$

Carbon dioxide is a colorless, odorless gas. It has a specific gravity of 44. It is about 1.5 times as heavy as air, and may therefore be poured downward into a vessel filled with air. It is ordinarily inert chemically, being uninflammable, and incapable of supporting the combustion of ordinary combustibles. A burning taper plunged into a vessel containing carbon dioxide is extinguished.

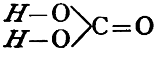
Carbon dioxide exists free in the atmosphere, of which it forms ordinarily three hundredths of one per cent. by volume. The air, in regions where large quantities of coal or other carbonaceous fuel are burned, may contain a considerably larger amount of carbon dioxide. Carbon dioxide is a product of animal respiration, and consequently the air of crowded rooms, which has become close and "stuffy," may contain as high as one tenth of one per cent. by volume of carbon dioxide. The leaves of living plants, however, through the agency of the green *chlorophyl* which they secrete, possess the property of absorbing carbon dioxide and assimilating the carbon, while exhaling the oxygen, thus restoring to the air the oxygen removed by combustion and animal respiration. In coal mines large quantities of carbon dioxide sometimes collect in the lower levels, where it is known as *choke damp.* Although carbon dioxide is not poisonous, air containing a few per cent. of carbon dioxide will produce suffocation.

At its critical temperature, 30.9°, carbon dioxide requires a pressure of 77 atmospheres to liquefy it, this being therefore its critical pressure. At the ordinary atmospheric temperature, carbon dioxide may be liquefied by a pressure of from 50 to 60 atmospheres. Liquid carbon dioxide is light, colorless, and mobile. When liquid carbon dioxide, held in a vessel under pressure, is allowed to escape into air under ordinary pressure, part of it volatilizes and part solidifies to a white snowy mass of solid carbon dioxide, which vaporizes slowly in the air, producing a temperature of − 78° at ordinary pressure. When liquid carbon dioxide, confined in a glass tube, is further cooled by a mixture of the snowy solid carbon dioxide and ether, it forms a transparent icelike mass, which will melt at about − 60°. Liquid carbon dioxide is commonly confined in wrought-iron cylinders, and finds use in many technical operations.

At ordinary temperature and at any pressure carbon dioxide will dissolve in water to an amount nearly equal in volume to that of the water. Since, however, the amount of a gas in a given volume varies directly as its pressure, it follows that at a given temperature the weight of carbon dioxide held in a solution is proportional to the pressure under which the solution is made. When the pressure of such a solution is lowered, some of the dissolved carbon dioxide escapes. The so-called *soda water* or *carbonated water*, and *champagne*, and some other wines, contain carbon dioxide under pressure, and the effervescence of such liquids when the pressure is released is due to the escape of the carbon dioxide. Many natural *spring waters* contain carbon dioxide in solution under pressure.

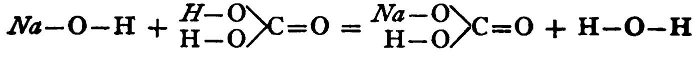
Carbonic Acid; Carbonates.

The solution of carbon dioxide in water acts like an unstable dibasic acid. So we name it *carbonic acid*, and assume for the solution the symbol



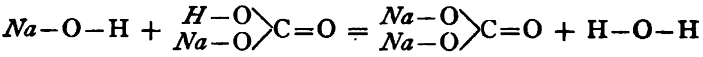
$$\begin{matrix} H-O \\ H-O \end{matrix}\!\!>\!C=O$$

Carbonic acid interacts readily with strong bases with the formation of water and neutral or acidic carbonates in which carbon is in the negative ion. Thus, carbonic acid forms with sodium hydroxide soluble acidic *sodium hydrogen carbonate*, $NaHCO_3$,



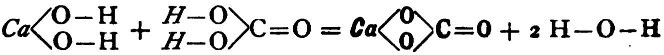
$$Na-O-H + \left.\begin{matrix}H-O\\ H-O\end{matrix}\right>C=O = \left.\begin{matrix}Na-O\\ H-O\end{matrix}\right>C=O + H-O-H$$

and then, by the further action of sodium hydroxide on the acidic carbonate, soluble neutral *sodium carbonate*, Na_2CO_3, results.



$$Na-O-H + \left.\begin{matrix}H-O\\ Na-O\end{matrix}\right>C=O = \left.\begin{matrix}Na-O\\ Na-O\end{matrix}\right>C=O + H-O-H$$

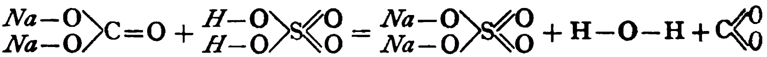
Many insoluble carbonates may be similarly formed. Thus, when carbonic acid is added to a solution of calcium hydroxide, insoluble *calcium carbonate*, $CaCO_3$, is formed as a white precipitate.



$$Ca\left<\begin{matrix}O-H\\ O-H\end{matrix}\right. + \left.\begin{matrix}H-O\\ H-O\end{matrix}\right>C=O = Ca\left<\begin{matrix}O\\ O\end{matrix}\right>C=O + 2\,H-O-H$$

If the carbonic acid is added to the calcium hydroxide in very small amount, as when clear limewater is allowed to stand in the air of a living room, the precipitate produces an incrustation on the surface of the limewater; and when air from the lungs is allowed to bubble through clear limewater the precipitate is formed, and produces a turbidity in the limewater.

Many of the *carbonates* are decomposed by heat with the liberation of carbon dioxide and the formation of the oxide of a positive element. We have already seen how calcium carbonate will break down into carbon dioxide and calcium oxide when strongly heated. The soluble carbonates probably undergo in water a slight hydrolysis, and to this fact we may attribute the alkaline reaction of the alkali carbonates, both neutral and acidic. The carbonates are generally decomposed by common acids with the liberation of carbon dioxide and the formation of salts of the respective acids. Thus, sodium carbonate is decomposed by sulphuric acid,



$$\left.\begin{matrix}Na-O\\ Na-O\end{matrix}\right>C=O + \left.\begin{matrix}H-O\\ H-O\end{matrix}\right>S\left<\begin{matrix}O\\ O\end{matrix}\right. = \left.\begin{matrix}Na-O\\ Na-O\end{matrix}\right>S\left<\begin{matrix}O\\ O\end{matrix}\right. + H-O-H + C\left<\begin{matrix}O\\ O\end{matrix}\right.$$

and by nitric acid, and by hydrochloric acid, in similar manner.

Many of the carbonates, especially calcium carbonate and magnesium carbonate, constitute important minerals, and occur naturally in large quantities as constituents of the rocks of the earth's crust. We have already studied the carbonates of sodium, potassium, magnesium, calcium, strontium, and barium, and later, in the secondary series, we shall find still other important carbonates.

Carbon Monoxide. *Carbon monoxide may be made by partially oxidizing carbon, by burning it in less than an excess of air or oxygen, or by heating it with a suitable oxide.* When charcoal or coke burns in less than sufficient oxygen to effect its complete oxidation, *carbon monoxide*, CO, is formed. It is an unsaturated compound, containing in each molecule only half the maximum amount of oxygen with which the carbon can combine.

$$2\,\mathrm{C} + \mathrm{O{=}O} = 2\,\mathrm{C{=}O}$$

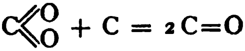
Carbon monoxide is also produced when steam is passed over carbon heated to redness, or when an electric spark is passed between carbon electrodes under water,

$$\mathrm{H{-}O{-}H} + \mathrm{C} = \mathrm{C{=}O} + \mathrm{H{-}H}$$

and it is generally produced when an oxide of a metal, such as copper oxide, CuO, is heated with carbon in proper proportion.

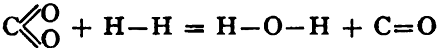
$$\mathrm{Cu{=}O} + \mathrm{C} = \mathrm{Cu} + \mathrm{C{=}O}$$

Carbon monoxide may also be formed by the partial reduction of carbon dioxide. Carbon monoxide is formed when carbon dioxide passes through a mass of carbon heated to incandescence.



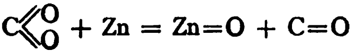
$$\mathrm{C}{<}^{\mathrm{O}}_{\mathrm{O}} + \mathrm{C} = 2\,\mathrm{C{=}O}$$

It is also produced when a mixture of carbon dioxide and an equal volume of hydrogen is passed through a tube heated to redness,



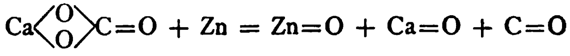
$$\mathrm{C}{<}^{\mathrm{O}}_{\mathrm{O}} + \mathrm{H{-}H} = \mathrm{H{-}O{-}H} + \mathrm{C{=}O}$$

and when carbon dioxide is passed through a tube containing a suitable metal, such as finely divided zinc heated to low redness.



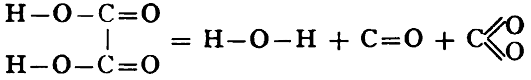
$$\mathrm{C}{<}^{\mathrm{O}}_{\mathrm{O}} + \mathrm{Zn} = \mathrm{Zn{=}O} + \mathrm{C{=}O}$$

Carbon monoxide may be set free from some compounds which contain carbon and oxygen. When calcium carbonate, which contains the elements of carbon dioxide, is heated with an equal quantity of zinc dust, carbon monoxide is evolved.



$$Ca\begin{matrix}O\\O\end{matrix}C{=}O + Zn = Zn{=}O + Ca{=}O + C{=}O$$

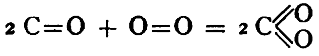
When oxalic acid, $H_2C_2O_4$, is heated strongly in the presence of sulphuric acid, which assists in removing the elements of water from the oxalic acid, a mixture of carbon monoxide and carbon dioxide is formed.



$$\begin{matrix}H{-}O{-}C{=}O\\ |\\ H{-}O{-}C{=}O\end{matrix} = H{-}O{-}H + C{=}O + C\begin{matrix}{=}O\\{=}O\end{matrix}$$

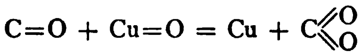
These methods are convenient for the preparation of carbon monoxide for laboratory purposes. In case the latter method be employed, the carbon dioxide formed may be removed by passing the mixed gases through a solution of sodium hydroxide.

Carbon monoxide is unsaturated and may be oxidized by burning in air or oxygen, or by heating with a suitable oxide, with the formation of carbon dioxide. When carbon monoxide is burned in air or oxygen, carbon dioxide is formed,



$$2\,C{=}O + O{=}O = 2\,C\begin{matrix}{=}O\\{=}O\end{matrix}$$

and when carbon monoxide is passed over copper oxide, CuO, heated to redness, carbon dioxide is formed and the copper oxide is reduced.



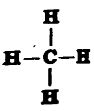
$$C{=}O + Cu{=}O = Cu + C\begin{matrix}{=}O\\{=}O\end{matrix}$$

The oxides of other metals may in a similar manner be reduced by carbon monoxide.

When coal or other carbonaceous fuel is burned in the presence of an excess of air, carbon dioxide is the only oxide formed, and at temperatures below 700° carbon dioxide is formed, whether the carbon be present in excess or not; but as the temperature of combustion increases the carbon dioxide is reduced when an excess of carbon is present, with the formation of increasing amounts of carbon monoxide, until at 1000° and above that temperature carbon monoxide is the principal oxide formed. In an ordinary grate fire the air, when first entering the burning coal or coke, causes its complete oxidation to carbon dioxide, which, passing up through the mass of ignited carbon, may become reduced to carbon monoxide, which either escapes with the other products of combustion or burns with a characteristic pale blue flame on the surface of the fuel.

$C{=}O$ *Carbon monoxide* is a colorless gas, possessing a faint odor, and burning in air or oxygen with a characteristic blue flame. A mixture of two volumes of carbon monoxide with one volume of oxygen explodes violently when ignited. The specific gravity of carbon monoxide is 27.99. One volume of carbon monoxide weighs 0.967 as much as an equal volume of air. It is only slightly soluble in water. At a temperature of — 141°, and under a pressure of 35 atmospheres, carbon monoxide forms a liquid which solidifies under 100 mm. pressure at — 207°, and which boils under 760 mm. pressure at — 190°. Carbon monoxide is poisonous when taken into the lungs, since it destroys the oxygen-carrying power of the hæmoglobin of the blood, forming with it a compound which exhibits a characteristic spectrum. The dangerous *after damp* produced by the explosion of a mixture of air and gaseous hydrocarbons (fire damp) sometimes found in coal mines consists of a mixture of carbon dioxide and carbon monoxide. Deaths are sometimes caused by the carbon monoxide from unventilated coal fires.

Hydrocarbons. *A great number of compounds of carbon with hydrogen, known under the general name hydrocarbons, are found naturally as the chief constituents of coal, petroleum, and other mineral products from which the hydrocarbons may be prepared by dry distillation.*



$$\begin{array}{c} H \\ | \\ H{-}C{-}H \\ | \\ H \end{array}$$

Methane, CH_4 (marsh gas), the most common of the hydrocarbons, is usually prepared for laboratory purposes by heating a mixture of sodium acetate, $Na(C_2H_3O_2)$, and sodium hydroxide.

$$Na(C_2H_3O_2) + NaOH = Na_2CO_3 + CH_4$$

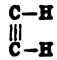
It may also be produced by the action of water upon aluminium carbide, Al_4C_3.

$$Al_4C_3 + 12\,H_2O = 3\,CH_4 + 4\,Al(OH)_3$$

Methane is a colorless, odorless gas, insoluble in water. Its specific gravity is 16.01. At a very low temperature and under great pressure it is a colorless liquid which at − 164° has a specific gravity of 0.415. When ignited, it burns with a faintly luminous flame, forming carbon dioxide and water.

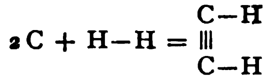
$$CH_4 + 2\,O_2 = 2\,H_2O + CO_2$$

Methane is formed when carbonaceous material, such as wood or coal or petroleum, is heated strongly out of contact with air. It is formed when vegetable matter decays under water, as frequently happens in swamps, and it collects in unventilated coal mines, where it produces *fire damp*. It forms an explosive mixture with air. In some localities, especially in regions rich in petroleum, it is formed underground and escapes from the earth in large quantities. It is a constituent of the commercial illuminating gas and of *natural gas*.



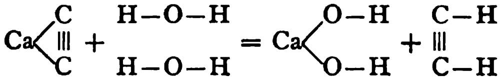
$$\begin{array}{l}C-H\\ |||\\ C-H\end{array}$$

Acetylene, C_2H_2, may be synthesized by passing an electric spark from one carbon terminal to another in an atmosphere of hydrogen.



$$2\,C + H-H = \begin{array}{l}C-H\\ |||\\ C-H\end{array}$$

For laboratory and commercial purposes, acetylene is prepared by the action of water upon calcium carbide, CaC_2.



$$Ca\begin{array}{l}\diagup C\\ \;|||\\ \diagdown C\end{array} + \begin{array}{l}H-O-H\\ \\ H-O-H\end{array} = Ca\begin{array}{l}\diagup O-H\\ \\ \diagdown O-H\end{array} + \begin{array}{l}C-H\\ |||\\ C-H\end{array}$$

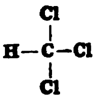
Acetylene is a colorless gas with a peculiar odor. At 1° and under 48 atmospheres' pressure it forms a colorless liquid which partially solidifies when brought under ordinary pressure. It is soluble in water. It burns readily in air, forming carbon dioxide and water.

$$2\,C_2H_2 + 5\,O_2 = 2\,H_2O + 4\,CO_2$$

When ignited in a small jet under suitable pressure and proper air supply acetylene burns with a dazzling white light that makes it useful for illuminating purposes. A mixture of 1 volume of acetylene with 12 volumes of air is a powerful explosive. Acetylene is produced when ordinary illuminating gas (coal gas) is only partially oxidized, as is the case when the gas flame in a Bunsen burner "snaps back" to the base of the burner, where the gas burns in less air than is sufficient for complete oxidation. Acetylene is also produced when carbonaceous material is heated out of contact with air, and small amounts are present in ordinary illuminating gas.

Besides methane and acetylene there are many other hydrocarbons which show striking similarities in constitution and properties. Like methane, CH_4, we have the similar compounds ethane, C_2H_6, propane, C_3H_8, butane, C_4H_{10}, and many others, which are all grouped together in the *methane series;* and like acetylene, C_2H_2, we have the similar compounds, methyl acetylene, C_3H_4, dimethyl acetylene, C_4H_6, and others which are grouped together in the *acetylene series.* Other hydrocarbons, including ethylene, C_2H_4, propylene, C_3H_6, butylene, C_4H_8, and other similar compounds, form the *ethylene series.* We have also benzene, C_6H_6, and many similar compounds forming the *benzene series* of hydrocarbons. The lowest members of all the series are gases, excepting benzene, which is a volatile liquid; higher members are liquids with boiling points which increase as the compounds ascend in the series; the highest members are solids, with melting points which increase as the compounds ascend in the series. Thus, in the methane series, the compounds from CH_4 to C_4H_{10} are gases under ordinary conditions, those from C_5H_{12} to $C_{15}H_{32}$ are ordinarily liquids, and $C_{16}H_{34}$ and those above it are ordinarily solids. The liquid hydrocarbons produced by the destructive distillation of carbonaceous material may be readily separated from one another by fractional distillation.

Hydrocarbon Derivatives. *By acting upon the hydrocarbons with suitable reagents many derivatives of the hydrocarbons may be formed.* The hydrogen atoms of the molecule of methane, CH_4, may be successively replaced with chlorine, forming chlorine derivatives of methane, CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4; and by similarly acting upon ethane, C_6H_6, we may obtain chlorine derivatives of ethane, C_2H_5Cl, $C_2H_4Cl_2$, etc. These chlorine derivatives differ from the hydrocarbons from which they are formed in the fact that they contain one or more atoms of chlorine in place of the same number of hydrogen atoms.



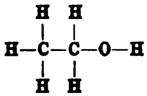
$$\begin{array}{c} Cl \\ | \\ H-C-Cl \\ | \\ Cl \end{array}$$

Trichlormethane, $CHCl_3$ (chloroform), the most important chlorine derivative of methane, may be separated from the mixture of chlorine derivatives formed when chlorine acts upon methane, CH_4.

$$CH_4 + 3\,Cl_2 = CHCl_3 + 3\,HCl$$

Chloroform is a very volatile colorless liquid, having a peculiar odor and a sweetish taste. It does not dissolve in water. It has a specific gravity of 1.5. It boils at 61.5°. It readily dissolves fatty and resinous substances. It acts as a powerful anæsthetic, and is largely used as such in surgery. It is produced commercially by heating calcium hypochlorite (bleaching powder) with alcohol.

By acting upon a chlorine derivative of a hydrocarbon with a hydroxide it is sometimes possible to replace the chlorine with a hydroxyl group, forming an alcohol, or hydroxyl derivative of the hydrocarbon.



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & O - H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

Ethyl hydroxide, C_2H_5OH (ethyl alcohol), the most important of the alcohols, may be formed in small quantities when monochlorethane, C_2H_5Cl (ethyl chloride), is heated with a dilute solution of sodium hydroxide, under pressure.

$$C_2H_5Cl + NaOH = C_2H_5OH + NaCl$$

Alcoholic Fermentation. Ethyl alcohol is ordinarily obtained by the *alcoholic fermentation* of certain carbohydrates, such as *glucose*, $C_6H_{12}O_6$ (dextrose, or grape sugar, etc.), in warm dilute solution, under the influence of an organized ferment found in *yeast* (*saccharomyces*), carbon dioxide being evolved.

$$C_6H_{12}O_6 = 2\,C_2H_5OH + 2\,CO_2$$

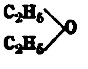
Certain carbohydrates, such as *sucrose*, $C_{12}H_{22}O_{11}$ (cane sugar), found in the sugar cane and in the sap of trees, *starch*, $(C_6H_{10}O_5)_n$, found in potatoes and grains, and *cellulose*, $(C_{12}H_{20}O_{10})_n$, which is the principal constituent of all woody fiber, when acted upon by common acids are changed into glucose, and may therefore be used for the manufacture of alcohol.

Ethyl alcohol, the ordinary alcohol of commerce, is a colorless mobile liquid, with a characteristic odor and a sharp taste. It has a specific gravity of 0.80. It boils at 78.3°, and becomes a solid at about —130°. It is very soluble in water. It is readily inflammable, burning with a pale hot flame, with the formation of carbon dioxide and water. Its vapor may form an explosive mixture with air.

$$C_2H_5OH + 3\,O_2 = 3\,H_2O + 2\,CO_2$$

When taken in small quantities alcohol may be assimilated in the animal body; in larger amounts it acts as an intoxicant and as a poison.

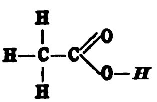
Many manufacturing industries are based upon the process of alcoholic fermentation. *Beer* and *wine* are formed by alcoholic fermentation under proper conditions of warmth, and in the presence of yeast, of solutions containing glucose or similar carbohydrates, derived from vegetable sources, and such liquors contain from 3 to 20 per cent. of alcohol. *Whisky* and *brandy* are formed by the distillation of fermented liquors, and may contain 50 per cent. of alcohol. In *bread making*, yeast is added to the dough, which is set aside in a warm place to permit the fermentation of a portion of the sugar and the liberation of carbon dioxide, which rising through the soft dough causes it to swell up into a porous, spongy mass. Sometimes *baking powder*, consisting of a mixture of compounds which will evolve carbon dioxide when heated to the temperatures of the oven, is added to dough to cause a more rapid evolution of carbon dioxide than is brought about by fermentation.



When ethyl alcohol, C_2H_5OH, is heated with sulphuric acid, it loses the elements of water and *ethyl oxide*, $(C_2H_5)_2O$ (ethyl ether), the common "ether" of commerce, is formed.

$$2\,C_2H_5OH = (C_2H_5)_2O + H_2O$$

Ethyl ether is a colorless mobile liquid of characteristic odor. It has a specific gravity of 0.736 at 0°. It boils at 35°. It is very volatile and is very inflammable. Its vapor may form an explosive mixture with air or oxygen. It is used largely as an anæsthetic and as a solvent for oils and resinous substances. Other ethers of similar constitution may be made from other alcohols.



When alcohols are partially oxidized they form acids, or carboxyl derivatives of the hydrocarbons, containing the carboxyl group, CO_2H. When ethyl alcohol, C_2H_5OH, is permitted to partially oxidize spontaneously, as, for example, when it is submitted to the action of air in contact with finely divided platinum, *acetic acid*, $CH_3 \cdot CO_2H$ or $H(C_2H_3O_2)$, is formed.

$$C_2H_5OH + O_2 = CH_3 \cdot CO_2\mathit{H} + H_2O$$

Acetic Fermentation.

Acetic acid is ordinarily formed by the *acetic fermentation* of ethyl alcohol in warm dilute solutions, under the action of a vegetable micro-organism, *mycoderma aceti*, which lives upon the oxygen of the air and nitrogenous and other material which may be present in the solution. Thus beer and fermented wines, which contain alcohol produced by the fermentation of sugar, get sour when exposed to warm air. The souring of milk, and of bread and pastry and other food stuffs, is due to the formation of acids by the excessive fermentation of the sugars contained in them. The common *vinegar* of commerce is made by the fermentation of cider or wine to which a mass of living ferment, known as the "mother of vinegar," is added. Acetic acid is manufactured in large quantities from the crude *pyroligneous acid* which is the most important product obtained by the dry distillation of wood.

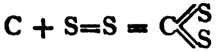
Acetic acid is ordinarily a colorless liquid. Below 16.7° it is a crystalline solid (glacial acetic acid), which has a specific gravity of 1.05. The liquid acid boils at 118°. It has a pungent odor, a sharp, sour taste, and a caustic action upon the skin. It readily mixes with water, alcohol, and ether, and will act upon many solids which are insoluble in water.

Acetic acid readily reacts with bases, with the formation of water, and salts known as *acetates*, which are generally soluble in water, and are readily decomposed by stronger acids. Thus, sodium hydroxide and acetic acid, $H(C_2H_3O_2)$, will interact to form *sodium acetate*, $Na(C_2H_3O_2)$.

$$NaOH + H(C_2H_3O_2) = Na(C_2H_3O_2) + H_2O$$

An important acetate is *lead acetate*, $Pb(C_2H_3O_2)_2$, a poisonous substance, used in medicine. Many other carbon acids similar to acetic acid are known.

Carbon Disulphide. *Carbon may combine directly with sulphur to form carbon disulphide.* When vapors of sulphur are passed over carbon heated to redness, the escaping vapors condense to form colorless liquid *carbon disulphide*, CS_2.



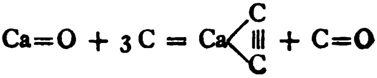
$$C + S{=}S = C{<}^{S}_{S}$$

Carbon disulphide is very volatile and has a characteristic odor. It boils at 47°. Its specific gravity is 1.29. It is insoluble in water. It dissolves caoutchouc and many resinous substances and oils. It burns readily with a blue flame, forming carbon dioxide and sulphur dioxide.

$$CS_2 + 3\,O_2 = CO_2 + 2\,SO_2$$

Carbon and nitrogen combine in the electric arc or under the influence of the induction spark to form *carbon nitride* or *cyanogen*, C_2N_2, so called because it enters into certain compounds of blue color. The cyanogen compounds will be considered in connection with our study of the compounds of nitrogen.

Carbides. We have already seen that carbon may be employed to effect the reduction of oxides of metals with the liberation of the metal in free condition, and the formation of carbon dioxide or carbon monoxide. If carbon is heated with certain oxides suitably selected at a temperature sufficiently high, such as that of the electric arc, the oxide will not only be completely reduced, but the element thus set free will combine with some of the excess of carbon, forming a *carbide* of the element. Thus, when a mixture of calcium oxide, CaO, produced by heating marble, is heated in an electric furnace with finely divided carbon, produced by charring sugar, a yellow crystalline residue of *calcium carbide*, CaC_2, is obtained.



$$Ca{=}O + 3\,C = Ca{<}\overset{C}{\underset{C}{|||}} + C{=}O$$

This compound is manufactured in less pure condition by heating together lime and coal or coke. It was first obtained by Wöhler, in 1862, by heating an alloy of calcium and zinc with carbon.

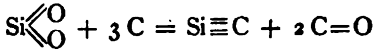
$$ZnCa + 2\,C = CaC_2 + Zn$$

Calcium carbide is ordinarily a gray crystalline solid of specific gravity 2.2. It is very readily decomposed by water with the formation of acetylene, C_2H_2,

$$CaC_2 + 2\,H_2O = Ca(OH)_2 + C_2H_2$$

and it is similarly acted upon by common acids. Since it was accidentally produced on a large scale by Wilson, in 1892, calcium carbide has been an important commercial product, and has led to a very general use of acetylene for certain purposes of illumination. *Barium carbide*, BaC_2, and *strontium carbide*, SrC_2, are similar to calcium carbide.

Another carbide, recently come into notice, is *silicon carbide*, SiC, or *carborundum*, now manufactured on a large scale by heating a mixture of silicon dioxide, SiO_2 (sand), with carbon (coke) and a flux of sodium chloride, in an electric furnace to a temperature of about 3500°.



$$Si\begin{matrix}\nearrow O\\ \searrow O\end{matrix} + 3\,C = Si{\equiv}C + 2\,C{=}O$$

Pure carborundum consists of brilliant green crystals, of specific gravity 3.22. It is not readily oxidized even when heated in oxygen. It is nearly as hard as diamond, and hence is valuable as an abrasive.

Boron carbide, B_6C, similar to carborundum, but exceeding it in hardness, consists of black shining crystals, of specific gravity 2.5. It is made by heating boron with carbon in an electrical furnace.

Aluminium carbide, Al_4C_3, may be obtained in the form of gray crystals by heating aluminium and carbon together in hydrogen in an electric tube furnace.

Organic Compounds and Organic Chemistry. *Since many compounds of carbon are either formed in living organisms or derived from substances produced by living organisms, the compounds of carbon in general are frequently called organic compounds, and the chemistry of the carbon compounds is known as organic chemistry.* Thus, we speak of ethyl alcohol, C_2H_5OH, as an *organic hydroxide*, and of acetic acid, $H(C_2H_3O_2)$, as an *organic acid*, both being *organic compounds*.

Summary. *Carbon dioxide and carbon monoxide are colorless gases, produced by burning carbon or by decomposing certain carbon compounds; carbon dioxide may be reduced to carbon monoxide; carbon monoxide may be oxidized to carbon dioxide. The solution of carbon dioxide in water, known as the unstable "carbonic acid," neutralizes bases with the formation of solid carbonates, some of which are soluble, all decomposed by the common acids, and all except the neutral alkali carbonates decomposed by heat with the liberation of carbon dioxide.*

The hydrocarbons, gaseous, liquid, and solid, are readily acted upon by reagents with the formation of many classes of derivatives, among which are the chlorides, the alcohols, the ethers, and the acids.

Carbon disulphide, a colorless liquid, is made by the combination of carbon with sulphur. The solid carbides are made by heating carbon with oxides of other elements, or with other elements, in an electrical furnace. Calcium carbide is decomposed by water with formation of acetylene.

The compounds of carbon are called organic compounds, and the chemistry of the carbon compounds is organic chemistry.

Industrial Applications. Carbon and its compounds find many useful applications in domestic economy, and in manufacturing. The diamond is prized as an ornament, graphite is employed as a lubricant and in lead pencils, and charcoal and coke are valuable fuels, while compacted amorphous carbon is used in making electrodes and battery plates. Some carbonates, particularly the limestones, are valuable building stones. The compounds of carbon which find most extensive application, however, are the hydrocarbons, which occur naturally in coal, petroleum, and natural gas, largely employed as fuel for the production of heat, power, and light. By the distillation of coal out of contact with air many other carbon compounds may be formed, some of which are of great value. Our knowledge of the properties of carbon and its oxides, and of some typical hydrocarbons and their derivatives, will help us to understand the preparation and utilization of carbon compounds on a large scale.

Fuels. The principal *fuels* are wood, and the mineral substances brown coal (lignite), bituminous coal, hard coal (anthracite), petroleum (coal oil), and natural gas. *Wood* consists essentially of *cellulose*, $(C_{12}H_{20}O_{10})_m$, as well as small quantities of resinous and gummy substances and water. The coals are largely complex mixtures of hydrocarbons. *Brown coal*, or *lignite*, is a dark brown or black substance of woody texture, containing from 50 to 80 per cent. of carbon, and from 15 to 20 per cent. of moisture. *Bituminous coal* is black, has a specific gravity of from

1.25 to 1.75, and contains from 70 to 90 per cent. of carbon. Those varieties containing large proportions of easily volatile matter have a dull luster, burn with a smoky flame, and often fuse together in a solid mass while burning. *Hard coal*, or *anthracite*, is black and very lustrous, has a specific gravity of about 1.75, and contains from 90 to 98 per cent. of carbon, and little readily volatile matter. It burns with little flame and with no smoke, and is more difficult to ignite than bituminous coal, though it burns readily in a current of air. It evolves more heat than is evolved by the same weight of other varieties of coal. The coals were probably formed by the slow decomposition of woody matter, containing cellulose, $(C_{12}H_{20}O_{10})_n$, under fresh water, with removal of carbon dioxide, CO_2, and marsh gas, CH_4, and subsequent compression of the residue with or without the action of heat. *Petroleum*, a dark yellowish or greenish oil, of specific gravity 0.8 to 0.9, may be burned without the production of smoke or soot, and produces over twice as much heat as an equal quantity of hard coal. *Natural gas* consists largely of methane, CH_4. It burns readily with a flame of low luminosity. It is the cheapest and most efficient fuel. The mineral fuels are found widely distributed in great abundance. In the United States, hard coal is found in Pennsylvania, and soft coal in Pennsylvania and in many Southern and Central states. Soft coal is found in abundance in England and throughout Europe generally. Petroleum is found in Pennsylvania, Texas, and in the central Western states, and in many other parts of the world. Natural gas occurs largely in the central Western states.

Distillation of Wood. When *wood* is heated out of contact with air, the cellulose, $(C_{12}H_{20}O_{10})_n$, which is its principal constituent, is decomposed, and several classes of products are formed. At temperatures between 160° and 275° acetic acid, $H(C_2H_3O_2)$, and similar products, known collectively as crude *pyroligneous acid*, are produced, while at higher temperatures hydrocarbons are the chief products, those distilling between 275° and 350° being gaseous, and those coming off between 350° and 450° being liquid and solid. By the modern method a series of iron *retorts*, connected with a condenser, and so arranged that the temperature may be readily controlled, has replaced the *charcoal kiln* of earlier times. The distillate produced separates into a light oily layer of the more volatile hydrocarbons, a reddish yellow or brown layer of pyroligneous acid, and a lower layer of black viscous wood tar. A residue of *charcoal* remains in the retort. By redistillation of the crude *pyroligneous acid* two products are obtained, *wood naphtha*, from which *methyl alcohol*, CH_3OH, (wood spirit), is made, and *wood vinegar*, from which *acetic acid*, $H(C_2H_3O_2)$, and acetates are prepared. By distilling the *wood tar*, *creosote* and *pitch* are produced.

Distillation of Coal. When coal is subjected to dry distillation several classes of products result: *gaseous hydrocarbons*, which are inflammable and may be used for *illuminating gas;* a liquid known as *gas* *liquor*, containing ammonium compounds and free ammonia; a strong-smelling black viscous residue known as *coal tar*, from which may be produced by fractional distillation and treatment with reagents many interesting *carbon compounds*, including alcohols, ethers, acids, and many valuable dyes and flavoring extracts; and a residue of *coke*, and in some cases the compacted "gas carbon," used for electrical purposes. When the coal is distilled for the purpose of producing coke, the gas liquor and coal tar may be saved as by-products, but the gases are burned as fuel to supply heat for the distillation. When the distillation is for the production of gas, heat is supplied from other fuel, and the gas liquor, coal tar, and coke are saved as by-products. The special consideration of the treatment of the gas liquor for the production of ammonia and ammonium compounds will be taken up under the subject of nitrogen and its compounds.

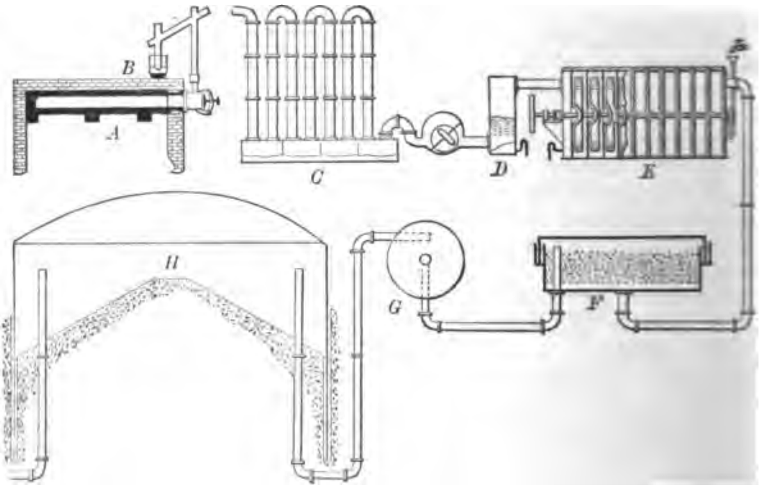


FIG. 11.—Manufacture of Illuminating Gas. (Adapted from Thorp.) *A*, Retort. *B*, Hydraulic Main. *C*, Condenser. *D*, Extractor. *E*, Scrubber and Washer. *F*, Purifier. *G*, Meter. *H*, Holder.

Coal Gas. For the production of *coal gas*, to be used for illuminating or other purposes, the raw material, usually bituminous coal, is heated in fire-clay *retorts* to from 1000° to 1200°, and the gaseous products of the distillation first pass into water, and then into cooled *condensing pipes* to condense and contain the heavier tar and oily products, and the soluble ammonium compounds. Thence the gas is pumped through *extractors*, *scrubbers*, and *washers* until it finally reaches the *purifiers*, which consist of shallow rectangular boxes, provided with false bottoms on which are spread thin layers of slaked lime or bog-iron ore, and thence into the holders, in which it is stored for use.

The slaked lime, $Ca(OH)_2$, serves to remove hydrogen sulphide, H_2S, carbon disulphide, CS_2, and carbon dioxide, CO_2, with the formation of various compounds of calcium, as is shown in the equations

$$Ca(OH)_2 + H_2S = CaS + 2\,H_2O$$
$$CaS + CS_2 = CaCS_3$$
$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$$

In case bog-iron ore, $Fe_2O_3 \cdot 3H_2O$, is employed as a purifier, only hydrogen sulphide is removed.

$$Fe_2O_3 \cdot 3\,H_2O + 3\,H_2S = 2\,FeS + S + 6\,H_2O$$

Another iron sulphide, Fe_2S_3, may also be formed in the process.

Water Gas. The manufacture of *water gas* for illuminating purposes consists in decomposing steam by incandescent carbon, with the formation of a mixture of carbon dioxide, hydrogen, and carbon monoxide, the *carbureting* of the mixture by the introduction of volatile hydrocarbons to give luminosity to the flame, and the removal of carbon dioxide and other impurities.

In the *Lowe process*, in which the gas is generated and carbureted in a single operation, anthracite coal or coke is burned to incandescence, in a vertical furnace or *generator*, in a blast of air, so regulated as to produce products of partial combustion, consisting principally of carbon monoxide and nitrogen, and known as *producer gas*. Chambers, called respectively the *carburetor* and the *superheater*, containing iron grills, are heated by burning in them the producer gas in an air blast, the resulting carbon dioxide and nitrogen being allowed to escape from the superheater into the air. When the proper temperature has been attained the air blast is cut off, and steam is injected into the generator, where it is decomposed by the incandescent coal or coke with the formation of the mixture of carbon dioxide, hydrogen, and carbon monoxide, known as *water gas*, which is inflammable, burning with great heat, but without luminosity.

$$C + 2\,H_2O = CO_2 + 2\,H_2$$
$$CO_2 + C = 2\,CO$$

To give the gas thus produced illuminating power a stream of petroleum is passed into the carburetors, where by contact with the hot checker work it is changed into gaseous products which, under the high temperature of the superheater, are resolved into ethane, C_2H_6, ethylene, C_2H_4, acetylene, C_2H_2, benzene, C_6H_6, and other hydrocarbons not readily condensible, and of high illuminating power. The gaseous mixture thus prepared is freed from carbon dioxide and other impurities by methods similar to those employed in purifying coal gas.

It is a common practice to mix coal gas with water gas for illuminating purposes, and the illuminating value of coal gas is frequently increased by the addition of a quantity of petroleum to the coal employed for distillation. Coal gas, under its ordinary pressure, and at its ordinary rate of flow, has been found to have an illuminating power equal to that of 17.5 standard candles, and it contains on the average 5 per cent. of illuminating hydrocarbons, 34.5 per cent. of methane, 49 per cent. of hydrogen, and 7.2 per cent. of carbon monoxide. Water gas, of 25 candle power, contains on the average 16.6 per cent. of illuminants, 19.8 per cent. of methane, 32.1 per cent. of hydrogen, and 26.1 per cent. of carbon monoxide. Because of the large proportion of carbon monoxide contained in it, water gas is very poisonous. Besides coal gas and water gas, *oil gas*, made by the direct distillation of petroleum,

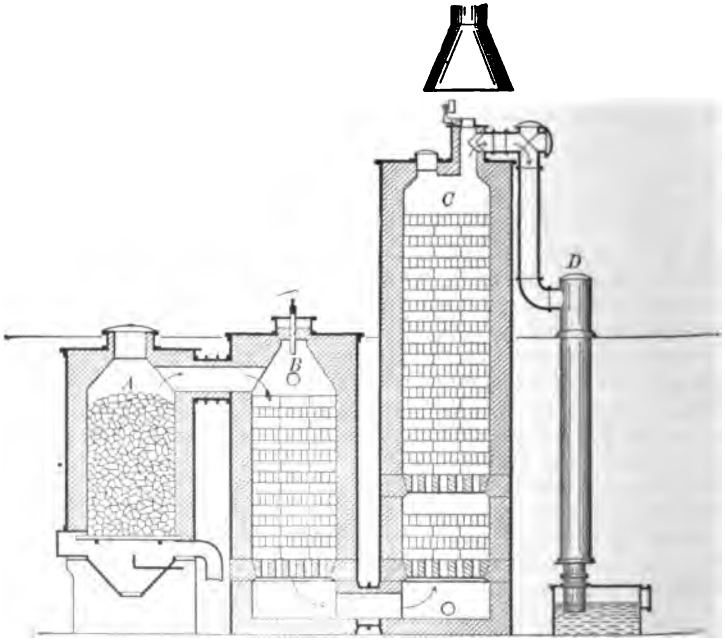


FIG. 12. — Manufacture of Water Gas. (Adapted from Thorp.) *A*, Generator. *B*, Carburetor. *C*, Superheater. *D*, Oil Heater and Seal.

acetylene, made by the action of water on calcium carbide, and *air gas*, made by mixing air in definite proportions with certain kinds of oil gas, are largely employed for illuminating purposes. In the incandescent burners, of the *Welsbach* type, the luminosity is increased by allowing the colorless flame of the Bunsen burner to impinge upon a gauze mantle made of the oxides of thorium and cerium, and other rare earths, which glow with great brilliance when heated.

Coal Tar Products. *Coal tar*, a by-product of the gas plant, is a viscous, black, oily, strongly smelling liquid, of specific gravity 1.15, of exceedingly complex composition. Tar is used to some extent as a preservative in coating timber, and in making tar paint and tar paper. When coal tar is submitted to fractional distillation, four sets of products are formed, — *light oil*, below 150°; the *middle oil*, from 150° to 210°; the *heavy oil*, from 210° to 270°, and *anthracene oil*, above 270°, while a residue of *pitch* is left behind. Upon distillation, the *light oil* yields hydrocarbons among which is *benzene*, C_6H_6, from which is made the *aniline*, $C_6H_5NH_2$, largely used in making artificial coloring matters. From the *middle oil* are produced *phenol* (C_6H_5OH) (carbolic acid) used in making dyes and high explosives, and valuable as an antiseptic in surgery, and *naphthalene*, $C_{10}H_8$, which serves as a basis for the preparation of a large series of dyes. The *heavy oil* is used as a preservative for timber and for making lampblack. The *anthracene oil* furnishes the *anthracene*, $C_{14}H_{10}$, of commerce, the basis of alizarin and other coloring matters.

Distillation of Petroleum. When crude *petroleum*, a mixture of hydrocarbons, is subjected to fractional distillation, the more volatile and inflammable oils pass over at the lower temperatures, and are followed by those of still higher boiling points, while a solid residue of waxy material is left in the retort. It is possible, however, to increase the production of the more volatile oils by conducting the last part of the distillation so that the heavy oils will be condensed within the retort, and drop back into the highly heated residue, where they will be decomposed or "cracked" into the more volatile products which readily pass over at lower temperatures. In the commercial process of petroleum refining, two distillates are produced, — the *benzene distillate*, which contains *gasolene* and other inflammable oils useful for solvent purposes and in varnish making, and the *burning oil distillate*, from which are produced by distillation and purification the different grades of *kerosene*. From the solid residues, *paraffin*, *lubricating oils*, *vaseline*, and *coke* are produced.

Flame. When hydrocarbons combine with oxygen under such conditions that they are completely and immediately converted into carbon dioxide and water, the mass of burning gas or *flame* is nearly colorless and only faintly luminous. Methane, CH_4, for example, burns from an ordinary gas burner with a faintly luminous flame.

$$CH_4 + 2\,O_2 = CO_2 + 2\,H_2O$$

Acetylene, C_2H_2, on the other hand, burns from an ordinary gas jet with a flame which is luminous, but very sooty from finely divided free carbon, the hydrogen burning first.

$$2\,C_2H_2 + O_2 = 2\,C_2 + 2\,H_2O$$

Burned from jets especially constructed to give great contact with air as the combustion proceeds, the acetylene burns with a flame intensely brilliant, and giving off no soot, though a piece of porcelain or metal placed within the flame becomes covered with soot.

$$2\,C_2H_2 + 5\,O_2 = 4\,CO_2 + 2\,H_2O$$

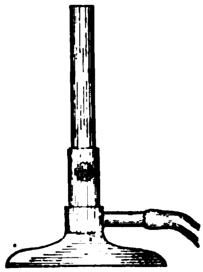


FIG. 13. — The Bunsen Burner.

As we look into the matter more closely it appears that the luminosity of the flame of burning hydrocarbons depends, under ordinary conditions, upon the presence in the flame of finely divided particles of carbon heated to a temperature of intense incandescence, and that a condition of luminosity may be brought about by adjusting the proportions of the constituents of the fuel — the carbon and the hydrogen — to one another and to the air supply. In methane the proportion of carbon to hydrogen is low, and from this gas, when burned from an ordinary gas jet, little carbon separates, even momentarily, to be heated by the extremely hot flame of the burning hydrogen. The *Bunsen burner* is so arranged that a regulated amount of air may be mixed with the gas before burning takes place, and in this burner the separation of free carbon and the luminosity of the flame may be produced at will. When the gas, unmixed with air, is allowed to burn only at the surface of contact with the surrounding air the fuel is in excess, the first stage of the oxidation is partial, and the flame is sooty; when air is mixed with the gas by means of the opening at the base of the burner, the combustion in the excess of oxygen is complete, and the flame no longer smokes, and, as the amount of air is increased, finally becomes non-luminous.

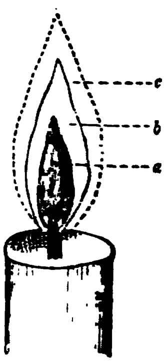


FIG. 14. The Candle Flame.

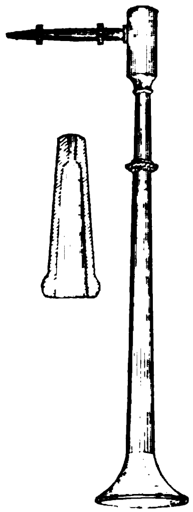


FIG. 15. — Blowpipe. (Platinum tip enlarged.)

The luminous flame of burning gas, best observed in a lighted candle, in which the hydrocarbons of the solid paraffin are melted, drawn up through the wick and volatilized at the point of ignition, consists of three zones, — an inner lower temperature zone (*a*) of unoxidized hydrocarbons, a middle luminous zone (*b*), where the hydrocarbons are partially oxidized and carbon is separated and heated to incandescence, and an outer almost invisible zone (*c*), in which the carbon and other products of the partial oxidation are completely oxidized to carbon dioxide and water. If a tube be inserted into the inner zone, the unchanged hydrocarbons may be removed from the flame and ignited. If a piece of porcelain or other cold object be introduced into the middle zone of the flame, soot will be deposited upon it, while introduced into the outer zone it will receive a deposition of water. The inner luminous zone, being rich in carbon, exerts a *reducing* action on substances brought into it, while the outer zone, containing heated air, exerts an oxidizing action. By means of a *blowpipe*, a convenient form of which consists of a tapering tube, bent at right angles, and provided with a mouthpiece and a platinum tip, pierced with a fine opening, either the reducing or the oxidizing action of the flame may be increased and manipulated so as to serve useful in the *blowpipe analysis* of minerals and other substances.

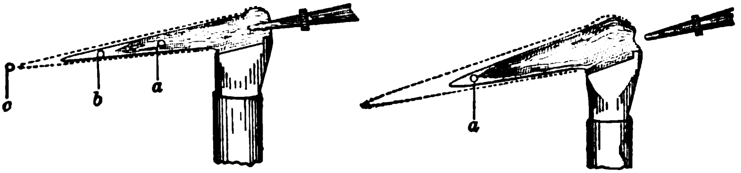


FIG. 16. — The Oxidizing Flame (blowpipe tip within the flame) and the Reducing Flame (blowpipe tip without the flame).

A gas flame, burning on one side of a wire gauze held horizontally across a stream of gas rising from a burner, may have its temperature so reduced by the heat-conducting material of the gauze as to prevent the ignition of the gas on the other side of the gauze. The *Davy safety lamp*, consisting of an oil lamp, the flame of which is entirely surrounded by a wire gauze, may be carried about in an atmosphere of inflammable gas, such as the fire damp of coal mines, without igniting the gas by contact with the flame.

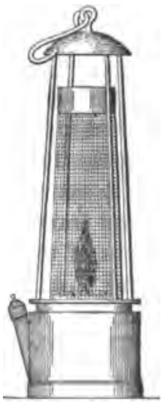
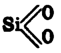


FIG. 17. The Davy Safety Lamp.

Silicon, Si, 28.4

Silica and Silicates.

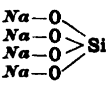
Silicon is found widely distributed in great abundance as silicon oxide or silica, SiO_2 (*quartz*), and in the *silicates*, or compounds of silicon with oxygen and other elements. We have already mentioned the *feldspars* (*orthoclase*, $KAlSi_3O_8$, *albite*, $NaAlSi_3O_8$, *anorthite*, $CaAl_2Si_2O_8$, etc.), the *micas* (*muscovite*, $H_2KAl_3Si_3O_{12}$, etc.), the white *kaolinite*, $H_4Al_2Si_2O_9$, from which we prepared aluminium compounds, and the red *garnet* and yellow *topaz*. These few examples are fairly typical of the great number of silicates which are found in rocks and soils.



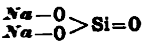
Silicon dioxide, or *silica*, SiO_2, occurs in nature in many varieties. Quartz, the most important form of silica, is found crystallized in hexagonal prisms and rhombohedrons, having a specific gravity of 2.6, and possessing a high degree of hardness. The purest form of quartz is the colorless *rock crystal*, while other varieties, colored by oxides of other elements, are known as *smoky quartz*, *rose quartz*, *amethyst quartz*, etc. *Agate*, *jasper*, and *onyx* are impure forms of quartz of varying luster and color. The ordinary white quartz crystals are found in great abundance either alone or in masses, or as a constituent of granite, gneiss, and syenite, and similar rocks. The rock formations known as *quartzite* and *sandstone*, as well as *sea sand*, consist principally of quartz. *Opal* is a colorless or variously colored amorphous and lighter form of silica, containing more or less water. *Silicious sinter*, a glassy natural form of silica, is deposited from the waters of certain hot springs, notably those of New Zealand, Iceland, and the Yellowstone region, which come to the surface charged with soluble silicates. Silica is also found imbedded in the woody structure of plants, particularly in the stems of the cereals and grasses, and it is also present in the feathers of some birds. Silica occurs also as *flint*, and in the microscopic animal remains known as *tripolite*.

The native silicon dioxide is insoluble in water, and is not acted upon by acids except hydrofluoric acid, but is acted upon by concentrated solutions of alkali hydroxides, and to some extent by alkali carbonates. Silica may be melted at the high temperature of the oxyhydrogen flame, or the electric furnace, when it forms a transparent glassy liquid.

Sodium Silicates. When silicon dioxide, SiO_2, is fused with sodium hydroxide, a product is formed the composition of which depends upon the proportion in which the substances interact. When one equivalent of silica interacts with four equivalents of sodium hydroxide, *sodium orthosilicate*, Na_4SiO_4, is formed.



$$SiO_2 + 4\,NaOH = Na_4SiO_4 + 2\,H_2O$$



$$\begin{matrix} Na-O \\ Na-O \end{matrix}\!>\!Si=O$$

With proportionately less sodium hydroxide *sodium metasilicate*, Na_2SiO_3, is the product formed.

$$SiO_2 + 2\,NaOH = Na_2SiO_3 + H_2O$$

The same compounds may be formed by the fusion of silicon dioxide with sodium carbonate, in suitable proportions and under suitable conditions of temperature.

$$SiO_2 + 2\,Na_2CO_3 = Na_4SiO_4 + 2\,CO_2$$

$$SiO_2 + Na_2CO_3 = Na_2SiO_3 + CO_2$$

In a similar manner, by fusing silicon dioxide with potassium hydroxide, or with potassium carbonate, in suitable proportions, we may obtain potassium metasilicate, K_2SiO_3. Potassium orthosilicate has never been prepared in a state of purity.

Polysilicates. Still other compounds, richer in silicon than the orthosilicates or the metasilicates, and known as the *polysilicates*, may be prepared by fusing silicon dioxide with suitable reagents. Thus, by the interaction, under conditions of fusion, of two equivalents of silicon dioxide with one equivalent of sodium hydroxide, *sodium disilicate*, $Na_2Si_2O_5$, may be obtained.

$$2\,SiO_2 + 2\,NaOH = Na_2Si_2O_5 + H_2O$$

With still higher proportions of silicon dioxide, *sodium trisilicate*, $Na_2Si_3O_7$, may be formed,

$$3\,SiO_2 + 2\,NaOH = Na_2Si_3O_7 + H_2O$$

with still higher proportions, *sodium tetrasilicate*, $Na_2Si_4O_9$,

$$4\,SiO_2 + 2\,NaOH = Na_2Si_4O_9 + H_2O$$

and even *sodium pentasilicate*, $Na_2Si_5O_{11}$, may be the product.

$$5\,SiO_2 + 2\,NaOH = Na_2Si_5O_{11} + H_2O$$

The same compounds may be produced by fusing silicon dioxide with sodium carbonate in the required proportions.

Similar *polysilicates* of potassium may be obtained by fusing silicon dioxide with potassium hydroxide or potassium carbonate in amounts larger than would be required for the formation of potassium metasilicate.

When silicon dioxide is acted upon by a concentrated solution of sodium hydroxide or of sodium carbonate, either the sodium orthosilicate, or the sodium metasilicate or one or more of the polysilicates may be formed according to the condition of concentration and the temperature of the solution. In the same manner, mixtures of the potassium silicates may be formed by acting upon silicon dioxide with solutions of potassium hydroxide or of potassium carbonate.

A mixture of sodium silicates, known commercially as *soluble soda glass*, is obtained as a glassy mass by heating together in proper proportions white sand, sodium carbonate, and charcoal, or by acting upon flint with a boiling solution of sodium hydroxide. When the product is powdered, it dissolves readily in water, forming a viscous liquid from which may be obtained crystals of the composition $Na_2Si_4O_9 \cdot 12\,H_2O$. Soluble soda glass is employed in frescoing and as a cement. A similar *soluble potash glass* may be made by methods similar to those employed for the production of the cheaper sodium product.

Silicic Acids. When a concentrated solution of a silicate is acted upon very gradually by an acid, a hydrogel is formed, the composition of which is variable. Thus, when we act upon a solution of sodium orthosilicate, with hydrochloric acid, the resulting precipitate may consist of the unstable *orthosilicic acid*, H_4SiO_4, corresponding in structure to sodium orthosilicate, Na_4SiO_4,

$$Na_4SiO_4 + 4\,HCl = \mathbf{H_4SiO_4} + 4\,NaCl$$

and the same unstable compound may be present in the precipitate formed by acting upon a solution of sodium metasilicate, Na_2SiO_3, with hydrochloric acid.

$$Na_2SiO_3 + 2\,HCl + H_2O = \mathbf{H_4SiO_4} + 2\,NaCl$$

Polysilicic Acids.

The orthosilicic acid cannot, however, be prepared in free condition, for when the precipitate is dried, it loses water, and the residue remaining has a composition dependent upon the conditions under which it is dried. Thus, when dried in a vacuum the residue has the composition of *metasilicic acid*, H_2SiO_3, corresponding to the sodium metasilicate already mentioned. When dried over sulphuric acid, or in air at definite temperatures, other oxyhydroxides corresponding in composition to the sodium polysilicates, and known as the *polysilicic acids*, may be formed. When the hydrogel is dried in air at ordinary temperature, the residue has the composition of *disilicic acid*, $H_2Si_2O_5$, and at higher temperatures we may get *trisilicic acid*, $H_2Si_3O_7$, *tetrasilicic acid*, $H_2Si_4O_9$, and *pentasilicic acid*, $H_2Si_5O_{11}$, corresponding in composition to the disilicate, trisilicate, tetrasilicate and pentasilicate of sodium respectively. All of these unstable compounds may be considered to be derivatives of orthosilicic acid, H_4SiO_4, from which they are formed by a process of *condensation* by the removal of water.

$$\underset{\text{(ortho)}}{H_4SiO_4} = \underset{\text{(meta)}}{H_2SiO_3} + H_2O$$

$$2\ \underset{\text{(meta)}}{H_2SiO_3} = \underset{\text{(di)}}{H_2Si_2O_5} + H_2O$$

$$\underset{\text{(meta)}}{H_2SiO_3} + \underset{\text{(di)}}{H_2Si_2O_5} = \underset{\text{(tri)}}{H_2Si_3O_7} + H_2O$$

$$\underset{\text{(tri)}}{H_2Si_3O_7} + \underset{\text{(meta)}}{H_2SiO_3} = \underset{\text{(tetra)}}{H_2Si_4O_9} + H_2O$$

$$\underset{\text{(tetra)}}{H_2Si_4O_9} + \underset{\text{(meta)}}{H_2SiO_3} = \underset{\text{(penta)}}{H_2Si_5O_{11}} + H_2O$$

When the hydrogel of silicic acid is heated strongly, all of the water of hydration may be driven off, and silicon dioxide may be formed as a finely divided white powder.

$$H_4SiO_4 = SiO_2 + 2\,H_2O$$

$$H_2SiO_3 = SiO_2 + H_2O$$

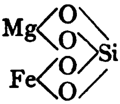
Such artificially prepared silica is more readily acted upon by concentrated solutions of alkali hydroxides or alkali carbonates than is quartz, the commonest natural form of silica.

When a large amount of the hydrochloric acid is added at once to solutions of the sodium silicates or potassium silicates, a considerable proportion of the silicic acid formed remains in solution, and in solutions sufficiently dilute no formation of the hydrogel takes place, the silicic acids formed remaining dissolved as a *hydrosol* in the water along with the sodium chloride which is formed simultaneously. The sodium chloride and the excess of hydrochloric acid may be removed from such a clear solution by *dialysis*. The non-crystallizable or colloidal silicic acid, being unable to pass through the porous wall of the dialyzer, will remain in the solution by itself until by concentration or addition of certain substances, like carbon dioxide or sodium carbonate, it forms the hydrogel.

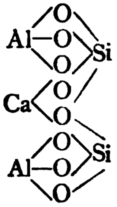
Mineral Silicates. Besides the silicates of sodium and of potassium which we have mentioned there are many other silicates, both artificial and natural, which have a composition analogous to that of the unstable orthosilicic acid, metasilicic acid, or the polysilicic acids. Although little is known of the true constitution of these more complex insoluble mineral silicates, we may for convenience classify them with the sodium silicates which they appear most nearly to resemble. Many mineral silicates have the composition of basic salts; many, like the so-called *zeolites*, are hydrated, containing water of crystallization. They are all similar to the sodium silicates in that they may be decomposed by acids, with the formation of a gelatinous precipitate of silicic acid.

Among the mineral silicates for which we may assume symbols corresponding to the different silicic acids we may mention several:

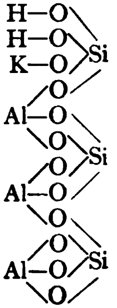
Orthosilicates



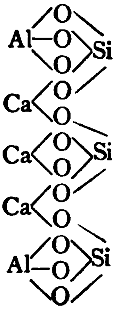
Chrysolite.



Anorthite.

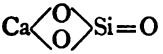


Muscovite.

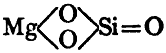


Garnet.

Metasilicates



Wollastonite.



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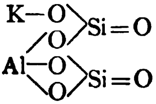

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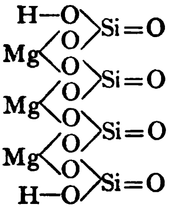
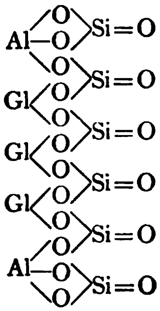
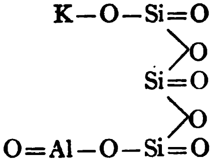


Talc.

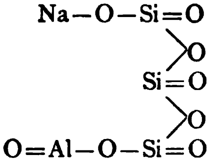


Emerald.

POLYSILICATES

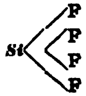


Orthoclase.



Albite.

Binary Compounds. *Certain binary compounds of silicon, in which silicon acts as a positive ion, may be made by acting upon silicon dioxide with suitable reagents.*



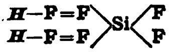
When hydrofluoric acid, HF, is allowed to act upon silicon dioxide, *silicon fluoride*, SiF_4, a colorless fuming gas of penetrating odor, is formed.

$$SiO_2 + 4\,HF = SiF_4 + 2\,H_2O$$

This compound is made most readily by warming a mixture of calcium fluoride, CaF_2 (*fluorspar*), silicon dioxide (sand), and sulphuric acid.

$$SiO_2 + 2\,CaF_2 + 2\,H_2SO_4 = SiF_4 + 2\,CaSO_4 + 2\,H_2O$$

In the action of hydrofluoric acid upon silicon dioxide we have the usual action of an acid upon an oxide to form a salt and water. In the ordinary mutual neutralization of a base with an acid the action is not reversible, — that is, the water formed is inert, and does not act upon the salt formed. In the case of the formation of silicon fluoride, however, and, as we shall see later, in the formation of many other binary compounds of weak positive elements, we find examples of salts which are hydrolyzed with the partial reversal of the reaction of neutralization by which they were formed.

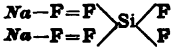


When silicon fluoride, SiF_4, is allowed to act upon water, it forms in solution a compound known as *hydrogen silicofluoride*, H_2SiF_6 (hydrofluosilicic acid), which is known only in solution, while the hydrogel of silicic acid separates.

$$3\,SiF_4 + 4\,H_2O = 2\,H_2SiF_6 + H_4SiO_4$$

A solution of hydrogen silicofluoride may be prepared by leading the gaseous silicon fluoride from the generator through a delivery tube into water contained in a glass cylinder, taking care to dip the end of the tube into mercury contained in the bottom of the cylinder, to prevent the end of the tube from becoming clogged by the hydrogel of silicic acid which is formed with the hydrogen silicofluoride. The gelatinous precipitate may be removed by filtration.

Hydrogen silicofluoride, H_2SiF_6, has a composition analogous to that of metasilicic acid, H_2SiO_3, differing from the latter compound in the fact that it contains six atoms of fluorine in the place of three atoms of oxygen. It is an acid and neutralizes bases with the formation of salts known as the *silicofluorides*. Thus, when we act upon sodium hydroxide with hydrogen silicofluoride, we obtain white fairly soluble *sodium silicofluoride*, Na_2SiF_6.

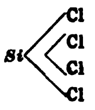


$$2\,NaOH + H_2SiF_6 = Na_2SiF_6 + 2\,H_2O$$

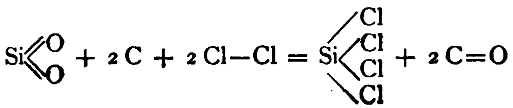
Many other silicofluorides are known, those of potassium, calcium, and barium being only slightly soluble in water.

When a solution of hydrogen silicofluoride is heated at low temperature it decomposes into hydrofluoric acid and silicon fluoride, SiF_4.

$$H_2SiF_6 = SiF_4 + 2\,HF$$



Silicon dioxide will not act upon hydrochloric acid to form a salt. When, however, a stream of chlorine is conducted over a mixture of silicon dioxide and carbon, heated to redness in a porcelain tube, *silicon chloride*, $SiCl_4$, is formed, which condenses to a colorless, fuming liquid, which boils at 59°.



$$Si{<}^{O}_{O} + 2\,C + 2\,Cl{-}Cl = SiCl_4 + 2\,C{=}O$$

The reduction of the silicon dioxide, which could not be effected by the action upon it of chlorine alone, is made easy by the presence of carbon. When water acts upon silicon chloride, hydrochloric acid and the hydrogel of silicic acid, H_4SiO_4, are formed.

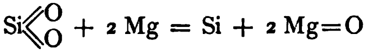
$$SiCl_4 + 4\,H_2O = H_4SiO_4 + 4\,HCl$$

Silicon bromide, $SiBr_4$, a colorless liquid, and *silicon iodide*, SiI_4, a colorless crystalline solid, may be prepared by methods similar to those employed to make silicon chloride.

Silicon chloroform, $SiHCl_3$, a volatile liquid, is known, as are also compounds of silicon with organic radicals, such as $Si(CH_3)_4$ and $Si(C_2H_5)_4$. Silicon also enters into the composition of various complex compounds of carbon.

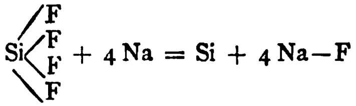
Other binary compounds of silicon are known, such, for example, as the solid substances, *magnesium silicide*, Mg_2Si, *silicon sulphide*, SiS_2, *silicon carbide*, SiC (carborundum), *silicon nitride*, Si_2N_3, and the gaseous *silicon hydride*, SiH_4, obtained by the action of hydrochloric acid upon magnesium silicide.

Silicon. When a mixture of silicon dioxide, SiO_2, and powdered magnesium is heated, *silicon* is produced as a brown amorphous powder.



$$Si{\ll}^{O}_{O} + 2\,Mg = Si + 2\,Mg{=}O$$

Silicon may also be obtained by heating silicon fluoride, SiF_4, with sodium.



$$Si\begin{matrix}F\\F\\F\\F\end{matrix} + 4\,Na = Si + 4\,Na{-}F$$

It was first obtained in pure condition by Berzelius in 1823 by heating potassium silicofluoride, K_2SiF_6, with potassium.

$$K_2SiF_6 + 4\,K = Si + 6\,KF$$

The amorphous silicon is readily oxidized to silicon dioxide when heated in air. A crystalline form of silicon, obtained as grayish black octohedra, of great hardness, by fusing sodium silicofluoride, Na_2SiF_6, with sodium and zinc, does not oxidize when heated in air, and is not attacked by ordinary acids. Silicon has a specific gravity of about 2.5.

It is acted upon by alkali hydroxides with formation of silicates of the alkali elements, and it combines with chlorine to form silicon chloride.

Summary. *Orthosilicic acid, formed by the action of acids upon native silicates, is not known in definite condition, although it may exist in solution and as a solid of unstable composition; metasilicic acid and certain other unstable oxysilicic acids known as polysilicic acids may be prepared as white solids; all the silicic acids may be decomposed by heating into silicon dioxide and water. Sodium orthosilicate, and the metasilicates and polysilicates of sodium and of potassium as well, may be prepared, all of which are white solids, many of them soluble in water, and readily decomposed by acids with the formation of a gelatinous, colorless precipitate from which metasilicic acid and the various polysilicic acids may be prepared. The silicates of elements other than the alkali elements are generally complex in composition, insoluble in water, and decomposed by acids with more or less difficulty.*

The gaseous silicon fluoride may be made by acting with hydrofluoric acid upon silicon dioxide, and is soluble in water with the formation of hydrogen silicofluoride, an acid which forms salts with strong bases; the liquid silicon chloride may be made by acting upon silicon dioxide with chlorine in the presence of carbon, and may also be formed by direct combination of silicon with chlorine.

Industrial Applications. The practical application of the silicon compounds consists in the utilization of the natural silicates, principally the clays, in the manufacture of *cement* and artificial stone, in making *ceramic wares*, such as the non-porous porcelain and stoneware, and the porous bricks, terra cotta, and common crockery, and in *glass making*. We shall briefly consider each of these important branches of industry.

Cement. *Cement* consists of a powdered mixture of certain complex anhydrous silicates and aluminates of calcium which possess the property of combining chemically with water, forming a compound of great hardness and permanence. Sometimes natural mixtures of silicates are found which only require fine grinding and admixture with lime to assume the property of hardening with water. The *pozzuolana cements*, made from silicates of volcanic origin found in Italy, and used since ancient times, are of this variety. Similar cements are sometimes made from blast furnace slags and from the ashes of certain kinds of coal. The so-called *Roman cements* are made by "burning" in kilns suitably selected limestones, which contain, besides calcium carbonate, suitable proportions of clay. The heating is continued at carefully regulated temperature until all the carbon dioxide is driven off, but is stopped before the mass is reduced to a state of fusion. The presence of magnesium compounds does not affect the value of these cements. In the United States the *Rosendale* cements, made from the clay limestone found in New York, is largely used. The more important *Portland cement*, an artificial product, is made by grinding and thoroughly mixing suitable proportions of calcium carbonate and clay rich in silica, and either drying and pressing the mixture into bricks, "burning" the bricks in specially constructed kilns in which coke or coal is used as a fuel, until the carbon dioxide is all driven out, and grinding the bricks to a fine powder; or else feeding the mixture into a rotary cylindrical kiln heated by gaseous fuel, or by powdered coal carried in an air blast, and grinding the continuously delivered product. When the powdered Roman or Portland cement is mixed with one third of its weight of water and a suitable quantity of sand, the water commences to combine with the cement, causing it to "set" or permanently harden, the rapidity of the hardening process depending upon the purity of the cement, the proportion of sand present, and the temperature of the water.

Ceramics. The manufacture of *ceramic wares* from clay depends upon the fact that when clay, which is a hydrated aluminium silicate, exceedingly plastic when moist, is heated, the water of hydration is driven off, and a hard, stone-like mass is left. The purest form of clay, the kaolin (*kaolinite*), or china clay, formed directly by the weathering of feldspar rocks, is of granular or crystalline structure, not very plastic when moist, and burns without shrinkage, forming white pottery. The *fire clays* are very infusible forms of kaolin, rich in silica, found underlying coal beds.

Porcelain. In the manufacture of *porcelain*, the most important porous ceramic, the mixed materials, which have been kneaded and set aside to age for a suitable time, are molded into any desired shape on a revolving horizontal table, known as the "potter's wheel," allowed to dry slowly at ordinary temperature, and then burned in an especially constructed kiln at low red heat until they cohere sufficiently to be glazed. The glazing is accomplished by dipping the article into a "glazing mixture," drying, and burning a second time in the kiln, by which the glaze, in a state of fusion, becomes more or less perfectly incorporated into the surface of the material. The hard *Berlin porcelain* has a body of kaolin, quartz, and feldspar, and is glazed at very high temperature with feldspar. The soft porcelains, like *English china*, *Sèvres ware*, and *Japanese ware*, consist of a body of kaolin mixed with other materials, and are glazed at lower temperature with a preparation of lead and boric acid. The cheaper porous *stoneware* is made of impure clays, often colored by iron oxide, and is glazed with sodium chloride, which coats the surface of the stoneware with fusible silicates. *Wedgwood ware* is an unglazed variety of stoneware.

Brick. In the manufacture of *brick*, another porous ceramic, common clay is allowed to stand exposed to the air for some months, then screened, mixed thoroughly with water in proper amount, and when necessary with other solid material, dried by exposure to air under cover, and finally "fired" to the required temperature in an open kiln, made of the air-dried brick, or in closed kilns of special construction. Wood or coal is usually employed as fuel. The cheaper grades of bricks, made from ordinary clay heated to about 1000°, are usually dark red, gray, or bluish in color, according to the amount of iron oxide, Fe_2O_3, formed in the heating, while some bricks, made of clays rich in compounds of calcium as well as of iron, are yellow or cream colored. The harder *paving bricks* are heated to from 1200° to 1300°, at which temperature they become partially fused. *Fire bricks* are made by heating compressed fire clay, to which silica has been added, to a very high temperature. Common *pottery*, another porous ceramic, is made of fusible clay, molded on a potter's wheel, heated in a kiln, and glazed. *Tiles* of many sorts are similarly made.

Glass. *Glass* is a non-crystalline transparent mixture of sodium silicate or potassium silicate with silicates of other elements, principally calcium and lead. In some kinds of glass, principally the colored varieties, compounds of various metals, such as iron, chromium, cobalt, and manganese, are present. Glass is hardly appreciably soluble in water, although it is slowly attacked by strong basic hydroxides. Ordinary acids do not affect it, although hydrofluoric acid acts upon it. Glasses which contain a high proportion of silicon are brittle, not readily attacked by reagents, and are difficult to fuse; while glasses containing a high proportion of sodium or potassium are less brittle, more readily decomposed, and are easily fusible. The principal substances used in glass making are silicon dioxide (white sand, powdered quartz, or sandstone), sodium carbonate (soda ash) or potassium carbonate (pearl ash), and either calcium carbonate (marble, limestone) or lead oxide (litharge), or red lead oxide, according to the kind of glass to be made. The raw materials are finely ground and thoroughly mixed, and then strongly heated in carefully constructed *fire pots* of fire clay until fusion results, when the temperature is suddenly raised to clear the mass of gases and solid particles, and then lowered until the mixture becomes pasty, when it is fit for working.

When colored glasses are desired, suitable oxides or salts of metals, or the metals themselves in finely divided condition, are added to the mixed material before the heating is commenced. Thus, ferrous oxide or chromous oxide give green glass, alkali sulphides give a yellow glass, cobaltic oxide or cupric oxide give a blue glass, and copper, cuprous oxide, or gold gives a red glass.

Plate glass is made by pouring the contents of the fire pot out on a flat, iron table, where it is rolled into the requisite size and thickness. Soda-lime glass is best adapted for casting and rolling. *Blown glass* is made by collecting a mass of molten glass on the end of an iron "pipe" and then blowing into the pipe from the lungs, shaping the resulting bubble of glass in the desired form either by dextrous movements of the pipe or by pressing into molds. Soda-lime glass is also well adapted for blowing. The ordinary *window glass* is made by blowing a mass of glass into a cylindrical form which is subsequently cut lengthwise and flattened out into a sheet. Glass utensils, such as drinking vessels, bottles, and lamp chimneys, are usually made of blown glass. All glass, whether cast into plates or blown, must be subjected to an *annealing process* by which the glass, in an especially constructed furnace, is allowed to cool very gradually for a considerable time to permit an equalization of tension throughout the mass. Glass which has been cooled without annealing is continually under internal stress, and will fly to pieces when slightly scratched, as may be readily shown by breaking the tail of a "Prince Rupert's drop." After annealing, the glass is burnished with sand and water, and is finally polished with emery or felt. *Cut glass* is made from a lead glass which is roughly shaped by blowing or pressing, and then cut into any chosen design by a revolving abrasive wheel.

TITANIUM, Ti, 48.1

Titanium is a constituent of many minerals of uncommon occurrence, notably the three varieties of native and differently crystalline *titanium dioxide*, TiO_2, known as *rutile*, *anatase*, and *brookite*. It occurs also combined in small amounts in many clays, in iron ore, and in *bauxite*, the ore from which aluminium is made. When the native and more or less impure titanium dioxide is fused with potassium hydrogen fluoride, KHF_2, and the mass extracted with boiling water containing hydrofluoric acid, HF, a solution is formed from which crystalline scales of *potassium fluotitanate*, $K_2TiF_6 \cdot H_2O$, which become anhydrous at 100°, separate out on cooling.

Titanium, in more or less pure form and probably containing some titanium nitride, is obtained by heating potassium fluotitanate with potassium. It is a gray powder, slightly acted upon by boiling water with evolution of hydrogen, oxidized to *titanium dioxide*, TiO_2, when heated in air, attacked by warm hydrochloric acid, by dilute hydrofluoric acid, nitric acid, and sulphuric acid, and capable when heated of combining directly with chlorine and with the nitrogen of air to form a nitride.

From a boiling solution of recrystallized potassium fluotitanate, ammonium hydroxide precipitates *titanic hydroxide*, $Ti(OH)_4$, which upon ignition yields pure *titanium dioxide*, TiO_2.

Titanic hydroxide, $Ti(OH)_4$, and titanium dioxide, TiO_2, are acted upon by sulphuric acid of suitable strength to form the sulphates,

$(TiO)SO_4 \cdot H_2O$, and $(TiO)SO_4$; while titanium dioxide acts upon fused sodium carbonate and fused potassium carbonate to produce *sodium metatitanate*, Na_2TiO_3, and *potassium metatitanate*, K_2TiO_3. So it appears that titanium enters into some compounds as a quadrivalent positive ion and into some others as a quadrivalent constituent of the negative ion.

Characteristic compounds of quadrivalent titanium are: *titanic hydroxide* or *titanic acid*, H_4TiO_4; *metatitanic acid*, H_2TiO_3, formed from titanic hydroxide at 120°, and even by drying over sulphuric acid; *titanium dioxide*, TiO_2, white, attacked by fairly strong and hot sulphuric acid, and more easily by hydrofluoric acid; liquid colorless *titanium tetrachloride*, $TiCl_4$, formed by the action of chlorine upon an ignited mixture of carbon and titanium dioxide, and at once hydrolyzed by water; the alkali fluotitanates, such as *potassium fluotitanate*, K_2TiF_6; the *metatitanates*, represented by the native minerals *perovskite*, $CaTiO_3$, and *ilmenite*, $FeTiO_3$, as well as by the alkali metatitanates, Na_2TiO_3, and K_2TiO_3; the *polytitanates* formed by more or less extensive hydrolysis of the alkali titanates, or by precipitation with an alkali carbonate of solutions, such as $K_2Ti_6O_{13} \cdot 3\,H_2O$, obtained by acting upon titanic hydroxide with an acid.

Titanium dioxide, TiO_2, when heated in hydrogen, gives black *titanium sesquioxide*, Ti_2O_3, corresponding to which is known violet-blue *titanium sesquichloride*, Ti_2Cl_6, obtained anhydrous by acting at 180° to 200° upon titanium tetrachloride, TCl_4, with finely divided silver, and dissolving to a violet-blue solution which is also formed by the action of a metal, like zinc, upon the solution of titanic hydroxide in hydrochloric acid or sulphuric acid. A still lower chloride, $TiCl_2$, is known. Certain compounds of titanium with nitrogen, titanium nitrides, TiN_2, and Ti_3N_4, are also of interest.

ZIRCONIUM, Zr, 90.6

Zirconium is found in many rare minerals, chiefly silicates, of which *zircon*, $ZrSiO_4$, is the most important. When finely powdered zircon is fused with potassium hydrogen fluoride, the mass pulverized and extracted with hot water, and the solution cooled, *potassium fluozirconate*, K_2ZrF_6, crystallizes out. Other fluozirconates are known, as *sodium fluozirconate*, Na_2ZrF_6, and *ammonium fluozirconate*, $(NH_4)_2ZrF_6$. *Zirconium* may be obtained by reducing fluozirconates by suitable metals. It occurs in allotropic forms: the amorphous form, a black powder, obtained by the action of potassium upon potassium fluozirconate; the graphitic form, made by the action of iron at 850° upon sodium fluozirconate; the crystalline form, hard steel-gray leaflets, made by fusing potassium fluozirconate with aluminium.

Heated in the air, zirconium oxidizes, the amorphous form burning, with formation of zirconium dioxide, ZrO_2. Normal zirconium hydroxide, $Zr(OH)_4$, is not definitely known, but *metazirconic acid*, H_2ZrO_3, white and voluminous, is precipitated when ammonium hydroxide acts upon the solution obtained by heating potassium fluozirconate with sulphuric acid, and this, when freshly precipitated, is attacked by strong acids, but is unaffected by alkali hydroxides.

Zirconium oxide, ZrO_2, white and powdery, is obtained by ignition of metazirconic acid. On fusion with alkali hydroxides or carbonates it forms *zirconates*, like *sodium metazirconate*, Na_2ZrO_3, which are hydrolyzed with formation of *polyzirconates*, like the *sodium zirconate*, $Na_2Zr_8O_{17} \cdot 12\,H_2O$. Zirconium dioxide is attacked by concentrated sulphuric acid, and from the solution may be obtained various salts, of which *zirconium sulphate*, $Zr(SO_4)_2$, and $Zr(SO_4)_2 \cdot 4\,H_2O$, are characteristic, as well as acidic and basic sulphates. So it appears that zirconium enters into compounds as a quadrivalent positive ion, while it may also be a quadrivalent constituent of the negative ion of certain salts.

Zirconium chloride, $ZrCl_4$, is formed as a white volatile sublimate when a mixture of zirconium dioxide with carbon is heated in dry chlorine; it dissolves in water with a hissing sound and forms a solution from which *zirconium oxychloride*, $ZrOCl_2 \cdot 8\,H_2O$, capable of yielding other oxychlorides on gentle heating, may be crystallized. *Potassium fluozirconate*, K_2ZrF_6, already mentioned, is a characteristic compound. The power to emit an intensely white and brilliant light when heated makes zirconium dioxide (zirconia) useful as a luminous material in the oxyhydrogen flame. It is also used as a constituent of the mantles of the Welsbach lights.

CERIUM, Ce, 140.25

Cerium occurs in several rare minerals and notably in *cerite*. By heating cerite with strong sulphuric acid, raising the mass to low redness, cooling, extracting with water, removing impurities by the acting with hydrogen sulphide and filtering, and precipitating by oxalic acid, the oxalates of cerium, lanthanum, praseodymium, and neodymium may be obtained. Upon igniting these oxalates, oxides are formed which are acted upon by hydrochloric acid, and from the resulting solution potassium hydroxide precipitates the corresponding hydroxides, which, acted upon by excess of chlorine, pass into solution, while reddish *ceric hydroxide*, $Ce(OH)_4$, more or less dehydrated, is formed and remains undissolved. Ceric hydroxide yields upon ignition yellowish *ceric oxide*, or cerium dioxide, CeO_2, and is acted upon by acids forming generally yellow salts like *ceric fluoride* or *cerium tetrafluoride*, $CeF_4 \cdot H_2O$, *ceric sulphate*, $CeSO_4 \cdot 4\,H_2O$, and some double salts, in all of which cerium is a quadrivalent positive ion.

When ceric hydroxide is treated with hydrochloric acid, chlorine is evolved, and cerous chloride, Ce_2Cl_6, is formed in solution. Upon evaporating this solution to dryness, cerous chloride is decomposed with evolution of hydrochloric acid and formation of an oxychloride. By adding ammonium chloride to the solution, and expelling it from the dried mass heated in a current of chlorine, white fusible anhydrous *cerous chloride*, Ce_2Cl_6, may be obtained.

Cerium is obtained by the electrolysis of cerous chloride as a steel-gray, lustrous, malleable metal, stable in the air at the ordinary temperature, but oxidizing with incandescence when heated.

Ceric salts are reduced by suitable agents, like sulphurous acid, H_2SO_3, to colorless cerous salts in which cerium is trivalent, such as *cerous sulphate*, $Ce_2(SO_4)_3$, which combines with different amounts of water, and forms double salts, with sodium sulphate and potassium sulphate, $Ce_2(SO_4)_3 \cdot 3\,Na_2SO_4 \cdot 2\,H_2O$, and $Ce_2(SO_4)_3 \cdot 3\,K_2SO_4 \cdot 2\,H_2O$, which are characteristically insoluble in concentrated solutions of alkali sulphates.

Colorless cerous salts are oxidized by various reagents to yellow ceric salts, and from solutions of cerous salts sodium hydroxide or potassium hydroxide precipitates white cerous hydroxide, which turns yellow slowly with oxidation and is converted on ignition in air to ceric oxide or *cerium dioxide*, CeO_2. The effectiveness of cerium dioxide as a constituent of the Welsbach mantle in intensifying the light emitted may depend upon the facility with which it is reduced and reoxidized, thereby acting as a catalyzer to cause rapid combustion and high temperature in the flame.

THORIUM, Th, 232.5

Thorium dioxide, long known as a constituent of certain rare minerals, is now found in abundance in the monazite deposit of North Carolina. *Monazite* may be decomposed by heating with sulphuric acid and raising the resultant mass to low redness. When the mass is extracted with water and the solution treated with oxalic acid, oxalates are precipitated from which ammonium oxalate forms soluble thorium ammonium oxalate. The addition of hydrochloric acid to the filtered solution precipitates *thorium oxalate*, $Th(C_2O_4)_2 \cdot 2\,H_2O$, which yields thorium dioxide on ignition.

Thorium dioxide, ThO_2 (thoria), white and powdery, is attacked by strong sulphuric acid, forming thorium sulphate, $Th(SO_4)_2$, which is soluble in cold water and crystallizes in colorless brilliant needles, $Th(SO_4)_2 \cdot 9\,H_2O$. From the water solution of thorium sulphate, ammonium hydroxide precipitates gelatinous *thorium hydroxide*, $Th(OH)_4$, readily attacked by acids with formation of salts in which thorium is a quadrivalent positive ion. A mixture of thorium dioxide with carbon yields, when ignited in a current of chlorine, sublimed thorium chloride, $ThCl_4$. Thorium hydroxide is acted upon by hydrochloric acid and from the solution crystals of thorium chloride, $ThCl_4 \cdot 8\,H_2O$, may be obtained. If the solution contains also potassium chloride, crystals of *potassium thorium chloride*, $KCl \cdot 2\,ThCl_4 \cdot 18\,H_2O$, separate, which may be dehydrated in a current of hydrogen chloride.

Thorium, a gray metallic powder, stable at ordinary temperatures, incandescent when heated, attacked by chlorine, bromine, iodine, and sulphur, acted upon by concentrated acids, is obtained by heating a mixture of anhydrous potassium thorium chloride with potassium.

Thorium dioxide is valuable as the chief constituent of the mantle of the Welsbach lamps, which may be made by saturating cotton fabric with a solution containing thorium nitrate and one or two per cent. of cerium nitrate, and burning away the organic fiber. The light emitted by the mantle of thorium oxide and cerium dioxide is extremely intense.

The compounds of thorium are radio-active, possessing the power of continually emitting Becquerel rays and radio-active emanations.

CHAPTER VIII

PRIMARY SERIES—GROUP V

Nitrogen, N, 14.04
Phosphorus, P, 31.0
Arsenic, As, 75.0
Antimony, Sb, 120.2
Bismuth, Bi, 208.5

Group V. THE elements of the fifth group of the primary series are, with the exception of phosphorus, found native in free condition, nitrogen in abundance, as the principal constituent of the *atmosphere*, and arsenic, antimony, and bismuth in lesser quantities as lustrous crystalline minerals. Phosphorus is never found native in free condition. All four elements occur in combination, nitrogen and phosphorus abundantly in some localities and other elements more sparingly.

Nitrogen. Nitrogen is an inert, colorless gas, combining with oxygen and hydrogen only when the mixed gases are acted upon by the electrical spark. In the nitrates and nitric acid, HNO_3, and in the nitrites, and the unstable nitrous acid, HNO_2, nitrogen is a negative ion. In the ammonium compounds, nitrogen is combined with hydrogen in a group, which in the decomposition of such compounds forms gaseous ammonia, which will combine with acids to form soluble "ammonium" salts. Ammonia dissolves in water to form a solution capable of neutralizing acids, like a fairly strong base. In the ammonium compounds nitrogen is a constituent of the negative ion. The most important naturally occurring nitrate is sodium nitrate, $NaNO_3$, known as *Chili saltpeter*, found in large deposits in South America. In certain volcanic regions ammonium chloride, NH_4Cl, "sal ammoniac," is also found native. The so-called *proteid* substances, which are present in the tissues of plants and animals, also contain nitrogen, and when such substances decay under certain conditions ammonium compounds and nitrates may be formed.

Phosphorus. Phosphorus exists in three allotropic modifications — a soft yellow solid, a reddish brown solid, and a black crystalline solid. It forms a stable oxide which combines with water to form a sirupy liquid hydroxide which is phosphoric acid, H_3PO_4. Phosphoric acid and the oxyacids which may be formed from it neutralize bases with the formation of *phosphates*, and similarly phosphorous acid neutralizes bases to form *phosphites*. In the phosphates and phosphites, and their corresponding acids, phosphorus is a constituent of the negative ion. In the case of a few rare compounds, analogous to the ammonium compounds, phosphorus with hydrogen forms a group of elements which shows a tendency to combine with acids as does ammonia. The chief native compounds of phosphorus are the *phosphates*, the most important being tricalcium orthophosphate, $Ca_3(PO_4)_2$, which is present in "rock phosphate," and in animal bones, of which it is the chief constituent.

Arsenic, Antimony, Bismuth. Arsenic, antimony, and bismuth are lustrous solids of high specific gravity, and generally like metals in appearance. They form oxides and hydroxides, which are generally acidic in character, and more so as the amount of oxygen combined in them is greater, but which develop basic characteristics as the atomic weight increases. Thus there are the arsenious acids and arsenites, and arsenic acids and arsenates, in which arsenic is in the negative ion, and sulphides and chlorides of arsenic, in which arsenic is positive. All five elements of the group form binary compounds with hydrogen, chlorine, bromine, iodine, sulphur, and other elements. Arsenic is found native in free *arsenic*, *mispickel*, FeAsS, *arsenolite*, As_2O_3, *realgar*, AsS, and *orpiment*, As_2S_3. Antimony is found in *stibnite*, Sb_2S_3. Bismuth occurs in the minerals *bismuth ocher*, Bi_2O_3, and *bismuthinite*, Bi_2S_3.

The valence of the elements of the fifth group of the primary series as indicated in the binary compounds is generally III or V.

Nitrogen, N, 14.04

The Atmosphere. *Nitrogen*, a colorless, odorless gas, occurs free everywhere in our world as the principal constituent of *atmospheric air*, of which it forms about three fourths by weight, the other one fourth consisting of oxygen, together with small variable amounts of water, carbon dioxide, ammonia, and nitrogen oxides, and small constant amounts of the inert gases, argon, helium, neon, krypton, and xenon. The specific gravity of air is 28.95, while that of nitrogen is 28.02. When air is cooled to a temperature of – 140°, at the same time being subjected to a pressure of 75 atmospheres, it condenses to a colorless liquid of specific gravity 0.9951, which is much richer in oxygen than is atmospheric air, since it consists of liquid nitrogen and liquid oxygen, mixed in nearly equal proportions. When boiled at – 190° under ordinary pressure, this so-called "liquid air" loses nitrogen more rapidly than oxygen, until the liquid finally consists chiefly of oxygen. When nitrogen, unmixed with other gases, is cooled to – 146° and submitted to a pressure of 35 atmospheres, it forms a colorless liquid, of specific gravity 0.885 at – 194°, and which boils at – 194° under ordinary pressure, and solidifies at – 214°.

"Liquid Air."

Preparation of Nitrogen. Nearly pure nitrogen may be collected in free condition best by burning in a quantity of air contained in a closed space, an excess of some readily oxidizable substance, such as phosphorus, which will combine with the oxygen of the air, leaving a residual gaseous mixture consisting principally of nitrogen. For the continuous production of nearly pure nitrogen, a current of air may be passed through a concentrated solution of potassium hydroxide, to remove carbon dioxide; then through granulated calcium chloride, or concentrated sulphuric acid, to remove the water; and, finally, over copper, heated to redness, to remove the oxygen, when the residual gas will consist of 99 per cent. of pure nitrogen, the remaining 1 per cent. consisting of argon and the other inert gases. For the preparation of pure nitrogen recourse must be had to some one of the nitrogen compounds which will evolve pure nitrogen when decomposed by suitable means.

When ammonia, NH_3, is passed over copper oxide, copper, water, and free nitrogen are the products; when an oxide of nitrogen is passed over hot copper, nitrogen and copper oxide are formed. Convenient methods for getting free nitrogen in quantity from its compounds will be pointed out after we have become more familiar with the characteristic behavior of the nitrogen compounds.

Properties of Nitrogen. Nitrogen is uninflammable, will not support the combustion of other substances, and is generally inert chemically, combining with a few other substances only at high temperatures, such as may be obtained by the electric spark. When electrical discharges of high voltage are passed through mixtures of nitrogen and oxygen, gaseous nitrogen tetroxide, NO_2, is formed, which will act upon water to produce nitric acid, HNO_3, and nitrogen dioxide, NO. When a similar discharge is passed through a mixture of nitrogen and hydrogen, gaseous ammonia, NH_3, results, which dissolves in water, forming the solution known as ammonium hydroxide, NH_4OH, which neutralizes acids to form "ammonium" salts.

Nitrates and Ammonium Compounds. Traces of ammonium nitrate, NH_4NO_3, and of ammonium nitrite, NH_4NO_2, are sometimes present in the air and in rain water. In the solid crust of the earth, in a few localities, sodium nitrate, $NaNO_3$, occurs in vast deposits; and in soils rich in nitrogenous organic remains the nitrates of sodium and of other elements are, under favorable conditions, formed by a peculiar process of fermentation. Some growing plants, through the agency of their roots, absorb atmospheric nitrogen directly and assimilate it into their tissues, from which nitrates may be subsequently produced in the soil. Nitrogenous vegetable or animal matter, when subjected to putrefactive decomposition, yields ammonia. In this way ammonia is generated to form ammonium compounds in the soil. The vast amounts of vegetable matter laid away in former geological times, in the shape of coal and oil, yield upon distillation, beside the gases used for illumination and heating, a small proportion of ammonia, which is an important commercial product.

Oxides and Hydroxides. *From the native nitrates, and from ammonium compounds produced from natural sources, we may best obtain the many nitrogen compounds.* Sodium nitrate, $NaNO_3$ (Chili saltpeter), the most abundant natural nitrate, furnishes the cheapest source for the preparation of nitric acid. When sodium nitrate is acted upon by sulphuric acid, vapors are produced which may be condensed into liquid *nitric acid,* HNO_3, somewhat colored by nitrogen tetroxide, NO_2, produced by the dissociation of some nitric acid during the distillation. By the action upon nitric acid of suitably selected substances, many artificial *nitrates* may be formed. From nitric acid and the nitrates may be prepared several oxides and hydroxides of nitrogen. The nitrogen oxides, five in number, form a series, each member of which is richer in oxygen by a fixed amount than the member standing next below it; while there are three nitrogen hydroxides, corresponding to three of the nitrogen oxides respectively.

Thus we have:

OXIDES	HYDROXIDES
Nitrogen pentoxide, N_2O_5	Nitric acid, HNO_3
Nitrogen tetroxide, N_2O_4 and NO_2	———
Nitrogen trioxide, N_2O_3	Nitrous acid, HNO_2
Nitrogen dioxide, NO	———
Nitrogen monoxide, N_2O	Hyponitrous acid, $H_2N_2O_2$

We shall find that nitric acid, HNO_3, may be formed from nitrogen pentoxide, N_2O_5, and corresponds to it in composition; nitrous acid, HNO_2, similarly corresponds to and may be formed from nitrogen trioxide, N_2O_3. Nitrogen pentoxide and nitrogen trioxide are therefore anhydrides of nitric acid and nitrous acid respectively. We shall also find that certain salts exist which correspond in composition to nitric acids of the composition H_3NO_4 and H_5NO_5, and to a polymerized nitric acid, $(HNO_3)_n$. Hyponitrous acid, $H_2N_2O_2$, although not actually formed from nitrogen monoxide, N_2O, corresponds to that oxide in composition.

Nitrogen Oxides. *For purposes of study we may conveniently prepare the nitrogen oxides by decomposing nitric acid or nitrates, by heating or by the action of suitable reagents.*

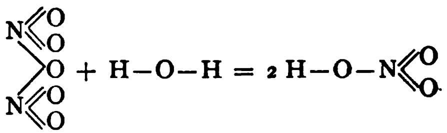
Nitrogen Pentoxide. *Nitrogen pentoxide*, N_2O_5, may be made by mixing cold concentrated nitric acid, HNO_3, and phosphorus pentoxide, P_2O_5, keeping the mixture cold during the reaction, and then distilling the nitrogen pentoxide by gentle heating.

$$2\ HNO_3 + P_2O_5 = 2\ HPO_3 + N_2O_5$$

It is a colorless, crystalline solid, melting at 30°, boiling at 47°, readily decomposing into oxygen and nitrogen tetroxide, NO_2.

$$2\ N_2O_5 = 2\ N_2O_4 + O_2$$

It combines with water to form *nitric acid*, HNO_3, with great evolution of heat.



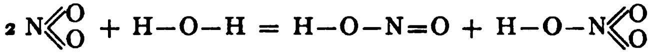
Nitrogen Tetroxide. *Nitrogen tetroxide*, N_2O_4 or NO_2, is usually prepared by heating perfectly dry lead nitrate, $Pb(NO_3)_2$, best mixed with an equal quantity of sand to prevent fusion of the mixture.

$$2\,Pb(NO_3)_2 = 2\,PbO + O_2 + 4\,NO_2$$

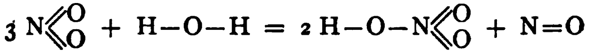
The heavy red gas evolved may be collected and condensed in a U-tube cooled by a freezing mixture of ice and salt.

Below 0° nitrogen tetroxide is a colorless liquid of specific gravity 1.49. At $-20°$ it is a colorless crystalline solid, melting at $-12°$. Above 0° the liquid assumes a yellow color, which deepens with rising temperature. At 26° the liquid boils, forming a yellowish brown gas, of specific gravity 76, which darkens in color, and assumes a lesser specific gravity with increase in temperature, until at 150° the gas has the specific gravity 46 and is dark red. The change in color and in specific gravity is due to the dissociation of the molecules of nitrogen tetroxide, which at 150° have a composition corresponding to the symbol NO_2, while at lower temperatures molecules of the form N_2O_4 appear to exist, although even at the boiling point of the liquid, 26°, about one third of the molecules have the simpler symbol, NO_2.

Nitrogen tetroxide will support the combustion of many substances. It will combine with water to form either *nitrous acid*, HNO_2, and *nitric acid*, HNO_3, or *nitric acid*, HNO_3, and nitrogen dioxide, NO, according to conditions of dilution and temperature.



$$2\,\mathrm{N}\begin{smallmatrix}/\!\!/\mathrm{O}\\ \backslash\!\!\backslash\mathrm{O}\end{smallmatrix} + \mathrm{H{-}O{-}H} = \mathrm{H{-}O{-}N{=}O} + \mathrm{H{-}O{-}N}\begin{smallmatrix}/\!\!/\mathrm{O}\\ \backslash\!\!\backslash\mathrm{O}\end{smallmatrix}$$



$$3\,\mathrm{N}\begin{smallmatrix}/\!\!/\mathrm{O}\\ \backslash\!\!\backslash\mathrm{O}\end{smallmatrix} + \mathrm{H{-}O{-}H} = 2\,\mathrm{H{-}O{-}N}\begin{smallmatrix}/\!\!/\mathrm{O}\\ \backslash\!\!\backslash\mathrm{O}\end{smallmatrix} + \mathrm{N{=}O}$$

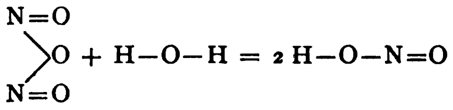
Nitrogen Trioxide. *Nitrogen trioxide*, N_2O_3, may be conveniently prepared by acting with a 50 per cent. solution of nitric acid, HNO_3, upon arsenic trioxide, As_2O_3, warming the mixture, and passing the reddish-colored fumes that are evolved into a U-tube, cooled to $-21°$ by a freezing mixure of ice and salt.

$$2\,HNO_3 + As_2O_3 = As_2O_5 + H_2O + N_2O_3$$

More or less nitrogen tetroxide, N_2O_4, is formed with the nitrogen trioxide, according to the conditions of temperature and the concentration of the nitric acid employed. Nitrogen trioxide forms a dark blue liquid of specific gravity 1.449 at 0°, boiling at 3.5°, and forming dark blue crystals at $-103°$. Above $-21°$ it begins to decompose into a mixture of nitrogen dioxide, NO, and nitrogen tetroxide, N_2O_4, which readily recombine when cooled, forming again the nitrogen trioxide.

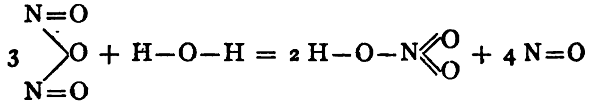
$$2\,N_2O_3 = N_2O_4 + 2\,NO$$

Nitrogen trioxide mixed with water in small quantities probably forms *nitrous acid*, HNO_2.



$$\begin{matrix}N{=}O\\ \quad\rangle O\\ N{=}O\end{matrix} + H{-}O{-}H = 2\,H{-}O{-}N{=}O$$

When warmed with water, it tends to produce *nitric acid*, HNO_3, and nitrogen dioxide, NO.



$$3\begin{matrix}N{=}O\\ \quad\rangle O\\ N{=}O\end{matrix} + H{-}O{-}H = 2\,H{-}O{-}N\langle\begin{matrix}O\\ O\end{matrix} + 4\,N{=}O$$

The reaction may consist first in the formation of nitrogen tetroxide, NO_2, and nitrogen dioxide, NO, and the subsequent combination of nitrogen tetroxide with water.

Nitrogen Dioxide. *Nitrogen dioxide*, NO (nitric oxide), is usually prepared by acting upon copper with dilute nitric acid.

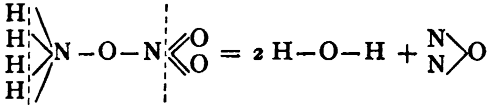
$$3\,Cu + 8\,HNO_3 = 3\,Cu(NO_3)_2 + 4\,H_2O + 2\,NO$$

Practically it may be prepared most conveniently by gradually adding concentrated sulphuric acid to a mixture of a saturated solution of sodium nitrate, $NaNO_3$, and copper turnings.

$$8\,NaNO_3 + 4\,H_2SO_4 + 3\,Cu = 4\,Na_2SO_4 + 3\,Cu(NO_3)_2 + 4\,H_2O + 2\,NO$$

The gas which is evolved in the cold is at first mixed with brown nitrogen trioxide, formed by the combination of the nitrogen dioxide with the oxygen of the air contained in the flask. After the first colored gases disappear, nearly pure nitrogen dioxide is evolved and may be collected over water. Nitrogen dioxide is a colorless gas, of specific gravity 30.06, only slightly soluble in water. At −93° and under a pressure of 71 atmospheres, it condenses to a colorless liquid which boils at −153.6°, and at −167° forms a white solid. Nitrogen dioxide supports the combustion of some substances which in burning evolve sufficient heat to cause the liberation of oxygen from the nitrogen dioxide. Thus, sulphur does not ordinarily burn in the gas, while charcoal and phosphorus burn in it if strongly kindled.

Nitrogen Monoxide. *Nitrogen monoxide*, N_2O (nitrous oxide, "laughing gas"), may be prepared by heating ammonium nitrate, NH_4NO_3, which breaks down at 170° into water and nitrogen monoxide.



$$\left.\begin{matrix}H\\H\\H\\H\end{matrix}\right\rangle N-O-N\left\langle\begin{matrix}O\\O\end{matrix}\right. = 2\,H-O-H+\left.\begin{matrix}N\\N\end{matrix}\right\rangle O$$

The gas, which is evolved rapidly, may be collected over warm water. The production of nitrogen monoxide takes place more quietly if, instead of ammonium nitrate, a mixture of sodium nitrate, $NaNO_3$, and ammonium sulphate, $(NH_4)_2SO_4$, be used.

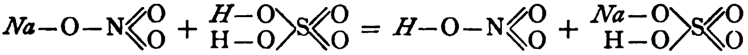
$$2\,NaNO_3 + (NH_4)_2SO_4 = Na_2SO_4 + 4\,H_2O + 2\,N_2O$$

Nitrogen monoxide is a colorless gas, of specific gravity 44.08, having a slight odor, soluble in water. At 38.8° and under a pressure of 775 atmospheres it becomes a colorless liquid, of specific gravity 0.937, boiling at −89.8° under ordinary pressure. When the liquid nitrogen monoxide is rapidly evaporated, a crystalline solid is formed, which melts at −102.3°. It supports the combustion of many substances. A mixture of equal volumes of nitrogen monoxide and hydrogen explodes when ignited, forming nitrogen and water. It is used as an anæsthetic.

Though nitrogen monoxide is soluble in cold water, its solution does not appear to possess acidic properties, and yet, as we shall see, by other means the acid, hyponitrous acid, $H_2N_2O_2$, of which nitrogen monoxide might naturally be supposed to be the anhydride, may be produced. This acid, moreover, may be decomposed to form nitrogen monoxide and water; but the reverse action, the formation of hyponitrous acid by union of nitrogen monoxide and water, does not take place.

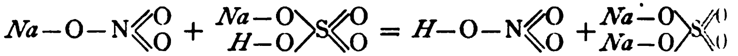
Nitric Acid. *In our study of the nitrogen hydroxides, which correspond to certain of the nitrogen oxides, we begin with nitric acid, the anhydride of nitrogen pentoxide, from which it may be made by the action of water.*

When we act upon sodium nitrate, $NaNO_3$, with a suitable amount of concentrated sulphuric acid, gently heating the mixture in a retort, vapors of *nitric acid*, HNO_3, are produced, which may be condensed in a vessel cooled by water to a nearly colorless liquid.



$$Na-O-N\left\langle\begin{matrix}O\\O\end{matrix}\right. + \left.\begin{matrix}H-O\\H-O\end{matrix}\right\rangle S\left\langle\begin{matrix}O\\O\end{matrix}\right. = H-O-N\left\langle\begin{matrix}O\\O\end{matrix}\right. + \left.\begin{matrix}Na-O\\H-O\end{matrix}\right\rangle S\left\langle\begin{matrix}O\\O\end{matrix}\right.$$

If the temperature be sufficiently high, the sodium hydrogen sulphate formed in the first stage of the reaction may be made to act upon more sodium nitrate to increase the product of nitric acid, although in this case some of the nitric acid is likely to be decomposed at the higher temperature.



$$Na{-}O{-}N\begin{matrix}\diagup O\\ \diagdown O\end{matrix} + \begin{matrix}Na{-}O\diagdown\\ H{-}O\diagup\end{matrix}S\begin{matrix}\diagup O\\ \diagdown O\end{matrix} = H{-}O{-}N\begin{matrix}\diagup O\\ \diagdown O\end{matrix} + \begin{matrix}Na{-}O\diagdown\\ Na{-}O\diagup\end{matrix}S\begin{matrix}\diagup O\\ \diagdown O\end{matrix}$$

For the *manufacture of nitric acid* on a large scale the sodium nitrate and sulphuric acid are mixed in an iron retort heated by a flame from below, and the vapors are condensed in a series of earthenware receivers. Upon mixing the resulting impure nitric acid with sulphuric acid and redistilling, nearly pure nitric acid is obtained.

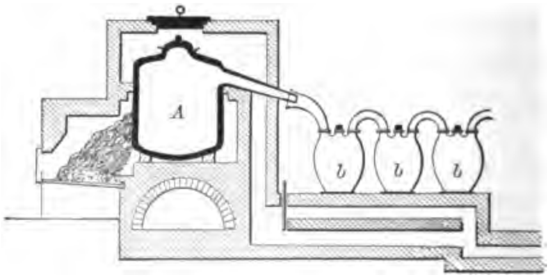
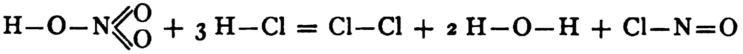


FIG. 18.—Manufacture of Nitric Acid. (Thorp.) *A*, Iron retort. *bbb*, Earthenware receivers.

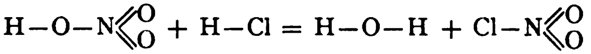
Ordinary pure *nitric acid* is a colorless, strong-smelling liquid, fuming strongly in air, of specific gravity 1.56, boiling at 86° with partial decomposition, and forming at −47° a crystalline solid. When a dilute water solution of nitric acid is distilled, the distillate, consisting at first of pure water, contains an increasing proportion of nitric acid, until at 121° under atmospheric pressure a mixture distils of constant composition containing 68 per cent. of nitric acid and corresponding to that of a mixture of a *trihydroxyl nitric acid*, H_3NO_4, and a *pentahydroxyl nitric acid*, H_5NO_5. This mixture, which is the ordinary concentrated nitric acid of commerce, has a specific gravity of 1.4 at 15°. It may be concentrated to a strength of 98.9 per cent. by mixing with a considerable proportion of sulphuric acid, redistilling at the ordinary atmospheric pressure, and blowing out the fumes of nitrogen tetroxide by means of dry air.

Nitric acid is very corrosive, staining the skin and other organic matter a bright yellow. Because of the large proportion of oxygen which it holds it is an effective oxidizer. It acts chemically upon nearly all metals except gold and platinum, and upon many other elements and compounds. It is largely used in metallurgical operations, and in making dyestuffs, guncotton, nitroglycerine, and other nitro-explosives.

Aqua Regia. A mixture of 1 volume of nitric acid with 4 volumes of hydrochloric acid, known since ancient times as *aqua regia*, is largely employed as a means for acting upon gold and platinum and other metals. The high oxidizing power and corrosive action of this mixture is due largely to the presence of chlorine, and of a compound of chlorine with nitrogen dioxide known as *nitrosyl chloride*, NOCl, and possibly of a compound of nitrogen tetroxide with chlorine, known as *nitroxyl chloride*, NO_2Cl.



$$H-O-N\begin{array}{l}\nearrow O\\ \searrow O\end{array} + 3\,H-Cl = Cl-Cl + 2\,H-O-H + Cl-N=O$$



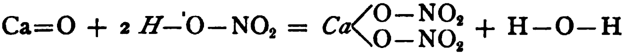
$$H-O-N\begin{array}{l}\nearrow O\\ \searrow O\end{array} + H-Cl = H-O-H + Cl-N\begin{array}{l}\nearrow O\\ \searrow O\end{array}$$

Nitrates. *Nitric acid may be neutralized by bases, with formation of water, and nitrates of positive elements in which nitrogen is a constituent of the negative ion.* Thus, when sodium hydroxide and nitric acid interact, *sodium nitrate*, $NaNO_3$, is formed.

$$Na-O-H + H-O-NO_2 = Na-O-NO_2 + H-O-H$$

We have already studied sodium nitrate and potassium nitrate. Many other nitrates may be formed in a similar way.

Nitrates may also be formed by the action of many oxides of positive elements upon nitric acid, with formation of water. Thus, calcium oxide, CaO, acts upon nitric acid to form *calcium nitrate*, $Ca(NO)_3$; and other nitrates may be formed similarly.



$$Ca=O + 2\,H-O-NO_2 = Ca\begin{array}{l}\nearrow O-NO_2\\ \searrow O-NO_2\end{array} + H-O-H$$

Nitric Acid and Metals. *Nitrates may be formed by the action of many positive elements upon nitric acid, with replacement of hydrogen, which generally acts upon the excess of nitric acid to form water and one or more products containing nitrogen.*

Nitric acid, like all other acids, contains replaceable hydrogen, and interacts with metals with the replacement of the hydrogen to form salts of the metal. But in the case of nitric acid the replaced hydrogen, instead of being set free, acts upon the excess of nitric acid with formation of water and a product of the reduction of nitric acid, the composition of which depends upon the concentration of the nitric acid employed and the temperature at which the reaction takes place. Thus zinc, which acts readily upon dilute sulphuric acid, hydrochloric acid, or acetic acid, with evolution of hydrogen, does not evolve hydrogen from nitric acid.

When we act upon concentrated nitric acid with zinc, there is a violent reaction, the zinc disappears, and *zinc nitrate*, $Zn(NO_3)_2$, is formed in solution, while dense clouds of reddish colored gas are evolved, which consist largely of nitrogen tetroxide, N_2O_4, and nitrogen trioxide, N_2O_3.

$$4\,HNO_3 + Zn = Zn(NO_3)_2 + 2\,H_2O + 2\,NO_2$$
$$6\,HNO_3 + 2\,Zn = 2\,Zn(NO_3)_2 + 3\,H_2O + N_2O_3$$

By the action of zinc upon fairly dilute solutions of nitric acid mixtures of the lower oxides, nitrogen dioxide, NO, and nitrogen monoxide, N_2O, and free nitrogen, are formed.

$$8\,HNO_3 + 3\,Zn = 3\,Zn(NO_3)_2 + 4\,H_2O + 2\,NO$$
$$10\,HNO_3 + 4\,Zn = 4\,Zn(NO_3)_2 + 5\,H_2O + N_2O$$
$$12\,HNO_3 + 5\,Zn = 5\,Zn(NO_3)_2 + 6\,H_2O + N_2$$

When the solutions upon which the zinc acts contain less than 10 per cent. of nitric acid, no nitrogen oxides or free nitrogen are produced, but *hydroxylamine*, NH_2OH, and *ammonia*, NH_3, products in which the replaced hydrogen is combined with the nitrogen of some nitric acid, may result.

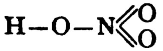
$$7\,HNO_3 + 3\,Zn = 3\,Zn(NO_3)_2 + 2\,H_2O + H_2NOH$$
$$9\,HNO_3 + 4\,Zn = 4\,Zn(NO_3)_2 + 3\,H_2O + NH_3$$

Many other metals, such as magnesium, copper, silver, and tin, may act upon nitric acid with formation of nitrates, water, and products of the reduction of nitric acid.

Properties of Nitrates. The *nitrates* formed by action of nitric acid upon basic oxides or hydroxides, or upon metals, are soluble in water. They are produced naturally by the slow oxidation under the influence of a vegetable organism, or *nitrifying ferment*, of nitrogenous matter in the soil, and this process has been applied artificially in the "niter plantations." The most important natural nitrate is sodium nitrate, $NaNO_3$, used as a source of potassium nitrate and as a fertilizer.

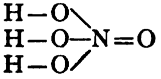
Basic Nitrates and Acidic Nitrates.

Certain basic nitrates of some of the less positive metals are known, which, ordinarily represented as oxysalts of monohydroxyl nitric acid,

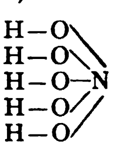


$$H-O-N\begin{smallmatrix}O\\O\end{smallmatrix}$$

may also be regarded as salts of *trihydroxyl nitric acid*,

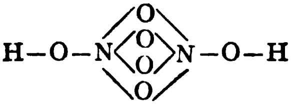


or of *pentahydroxyl nitric acid*,

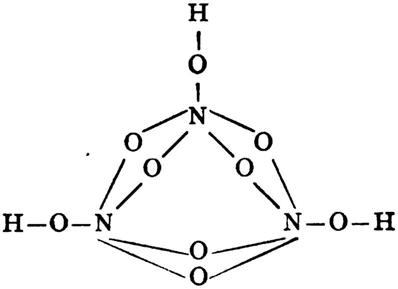


Such are the basic lead nitrate, $H_2Pb_2O_6(NO)_2$, the basic mercurous nitrate, $H_2Hg_2O_6(NO)_2$, and the basic lead nitrate, $H_4Pb_3O_{10}N_2$.

On the other hand, acidic nitrates such as $NH_4NO_3 \cdot HNO_3$, $RbNO_3 \cdot HNO_3$, $CsNO_3 \cdot HNO_3$, and $KNO_3 \cdot 2\,HNO_3$, $NH_4NO_3 \cdot 2\,HNO_3$, as well as double nitrates, such as $KNO_3 \cdot AgNO_3$, $NH_4NO_3 \cdot AgNO_3$, and others more complex, may be regarded as derivatives of polymerized nitric acids, $(HNO_3)_n$, such as

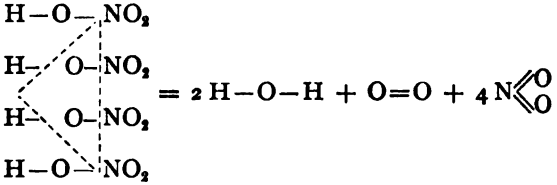


and



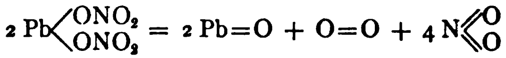
Decomposition of Nitrates.

Both nitric acid and the nitrates may be decomposed by heating. When the ordinary concentrated nitric acid, containing a small proportion of water, is distilled, some of it is decomposed with the formation of nitrogen tetroxide, which gives to the acid a characteristic yellow color. A similar decomposition takes place when ordinary nitric acid is allowed to stand in sunlight. When we heat nitric acid in a sealed tube to 260°, it breaks up completely into water, oxygen, and nitrogen tetroxide, NO_2.



$$\begin{array}{l} H-O-NO_2 \\ H-O-NO_2 \\ H-O-NO_2 \\ H-O-NO_2 \end{array} = 2\,H-O-H + O=O + 4\,N\left\langle\begin{array}{l}O\\O\end{array}\right.$$

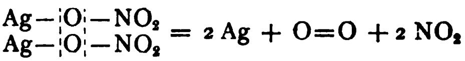
Many nitrates behave similarly, but the products formed in the decomposition depend upon the nature of the positive ion of the nitrate. When lead nitrate, $Pb(NO_3)_2$, is heated, oxygen and nitrogen tetroxide, NO_2, may be evolved, lead oxide, PbO, which is not readily broken up by heat, being left behind.



$$2\,Pb\left\langle\begin{array}{l}ONO_2\\ONO_2\end{array}\right. = 2\,Pb=O + O=O + 4\,N\left\langle\begin{array}{l}O\\O\end{array}\right.$$

Calcium nitrate, $Ca(NO_3)_2$, cupric nitrate, $Cu(NO_3)_2$, and the nitrates of certain other elements forming stable oxides, decompose similarly when heated.

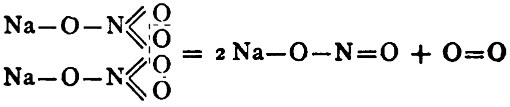
When silver nitrate, $AgNO_3$, is heated, nitrogen tetroxide, NO_2, and oxygen are evolved, and silver remains as a residue. Silver oxide, AgO, being readily decomposed by heating, cannot be left behind.



$$\begin{array}{l} Ag-O-NO_2 \\ Ag-O-NO_2 \end{array} = 2\,Ag + O=O + 2\,NO_2$$

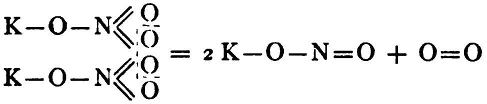
Mercuric nitrate, $Hg(NO_3)_2$, when heated not too strongly, leaves mercuric oxide, HgO, but at a higher temperature the oxide is decomposed into mercury and oxygen.

Reduction of Nitrates. *The nitrates of the alkali elements when heated evolve oxygen, and form nitrites in which nitrogen is in the negative ion.* Thus, when sodium nitrate, $NaNO_3$, is strongly heated, oxygen is evolved, leaving a residue of *sodium nitrite*, $NaNO_2$.



$$\begin{array}{l} Na-O-N\left\langle\begin{array}{l}O\\O\end{array}\right. \\ Na-O-N\left\langle\begin{array}{l}O\\O\end{array}\right. \end{array} = 2\,Na-O-N=O + O=O$$

Potassium nitrate, KNO_3, may be similarly decomposed with the formation of *potassium nitrite*, KNO_2.



$$\begin{matrix} K-O-N\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix} \\ K-O-N\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix} \end{matrix} = 2\,K-O-N=O + O=O$$

Both sodium nitrate and potassium nitrate are good oxidizers, but potassium nitrate, since it is less hygroscopic than the naturally occurring sodium nitrate, is better adapted for such purposes. If we throw a piece of charcoal upon some molten potassium nitrate, the charcoal is ignited and burns fiercely.

$$4\,KNO_3 + 5\,C = 2\,K_2CO_3 + 3\,CO_2 + 2\,N_2$$

Gunpowder. The oxidizing power of potassium nitrate makes it a valuable constituent of *gunpowder*. The standard black gunpowder of the United States Army is composed of 75 per cent. potassium nitrate, 15 per cent. charcoal, 10 per cent. sulphur. When this powder is burned in an open space, it decomposes chiefly into potassium sulphide, carbon dioxide, and nitrogen.

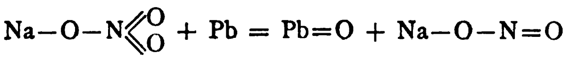
$$2\,KNO_3 + 3\,C + S = K_2S + 3\,CO_2 + N_2$$

When gunpowder is exploded under pressure in a confined space, a large number of gaseous products are formed, and the sudden expansion of these may give a pressure equal to many tons per square inch of surface.

Nitrous Acid and Nitrites. *Nitrous acid*, HNO_2, the lower hydroxide of nitrogen, corresponding to nitrogen trioxide, N_2O_3, from which it may be made by the action of water, is known only in unstable condition in solution, and is easily broken down to form nitric acid, nitrogen dioxide, NO, and water.

$$3\,HNO_2 = HNO_3 + 2\,NO + H_2O$$

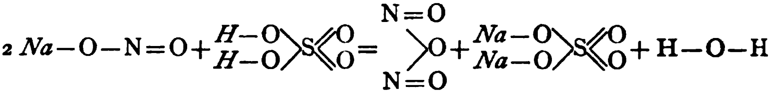
Certain nitrites are stable, well characterized, and soluble in water. We have already seen that *sodium nitrite*, $NaNO_2$, may be made by heating sodium nitrate. Sodium nitrite may be prepared more readily by heating sodium nitrate with some reducing agent such as lead, which will become oxidized at the expense of the nitrate.



$$Na-O-N\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix} + Pb = Pb=O + Na-O-N=O$$

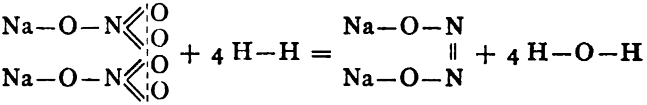
Potassium nitrite, KNO_2, may be similarly made by heating potassium nitrate, alone or with a reducing agent. The *nitrites* of the alkali elements are generally white crystalline solids. Sodium nitrite is largely employed in making certain dyestuffs containing nitrogen.

The nitrites are readily decomposed by acids, with formation of nitrogen trioxide. When sodium nitrite, $NaNO_2$, is acted upon by sulphuric acid, dense reddish fumes arise which consist principally of nitrogen trioxide, N_2O_3, sodium sulphate remaining in the solution.



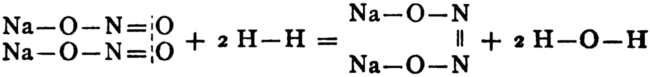
Hyponitrous Acid and Hyponitrites. *Hyponitrous acid*, $H_2N_2O_2$, the lowest hydroxide of nitrogen, corresponding to nitrogen monoxide, N_2O, and its salts, the *hyponitrites*, may be made by reducing nitrates and nitrites by suitable means.

When sodium nitrate is submitted to the action of nascent hydrogen, produced by electrolysis or by the action of sodium amalgam upon water, a residue of *sodium hyponitrite*, $Na_2N_2O_2$, is formed.



$$\begin{array}{l} Na-O-N\begin{smallmatrix}=O\\=O\end{smallmatrix} \\ Na-O-N\begin{smallmatrix}=O\\=O\end{smallmatrix} \end{array} + 4\,H-H = \begin{array}{r} Na-O-N \\ \Vert \\ Na-O-N \end{array} + 4\,H-O-H$$

Sodium nitrite may be similarly reduced by hydrogen.



$$\begin{array}{l} Na-O-N=O \\ Na-O-N=O \end{array} + 2\,H-H = \begin{array}{r} Na-O-N \\ \Vert \\ Na-O-N \end{array} + 2\,H-O-H$$

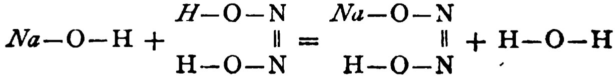
By acting upon sodium hyponitrite, $Na_2N_2O_2$, with silver nitrate, $AgNO_3$, *silver hyponitrite*, $Ag_2N_2O_2$, may be formed as a yellow powder.

$$Na_2N_2O_2 + 2\,AgNO_3 = Ag_2N_2O_2 + 2\,NaNO_3$$

The silver hyponitrite, $Ag_2N_2O_2$, may be acted upon by hydrogen chloride in solution in ether with formation of *hyponitrous acid*, $H_2N_2O_2$, as crystals, soluble in water.

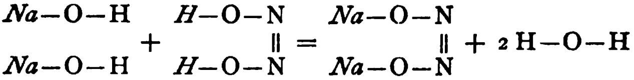
$$Ag_2N_2O_2 + 2\,HCl = H_2N_2O_2 + 2\,AgCl$$

Hyponitrous acid will neutralize sodium hydroxide, with formation of *sodium hydrogen hyponitrite*, $NaHN_2O_2$,



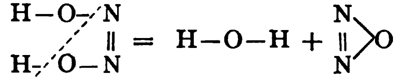
$$Na-O-H + \begin{array}{r} H-O-N \\ \Vert \\ H-O-N \end{array} = \begin{array}{r} Na-O-N \\ \Vert \\ H-O-N \end{array} + H-O-H$$

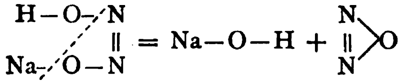
or *sodium hyponitrite*, $Na_2H_2O_2$.



$$\begin{matrix} Na{-}O{-}H & & H{-}O{-}N & & Na{-}O{-}N & \\ & + & \| & = & \| & +\ 2\,H{-}O{-}H \\ Na{-}O{-}H & & H{-}O{-}N & & Na{-}O{-}N & \end{matrix}$$

Both hyponitrous acid, $H_2N_2O_2$, and the hyponitrites, such as the sodium hydrogen hyponitrite, $NaHN_2O_2$, are very unstable, decomposing spontaneously, with formation of nitrogen monoxide, N_2O, as one of the products.

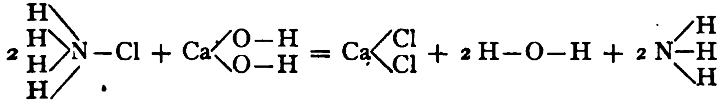




Ammonia and Ammonium Hydroxide.

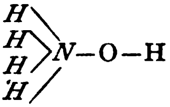
Ammonium chloride, the most common ammonium compound, may be used as a source of ammonia gas, and of the solution of ammonia in water, known as ammonium hydroxide.

When an ammonium compound is heated with a strong base, ammonia is set free. When we heat a mixture of equal weights of ammonium chloride, NH_4Cl, and calcium hydroxide, $Ca(OH)_2$, we get a rapid evolution of *ammonia*, NH_3, which may be collected by the downward displacement of air in a flask inverted over the delivery tube.

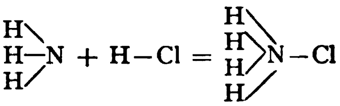


Ammonia is a colorless gas with a characteristic suffocating odor. At —40° under ordinary pressure it forms a colorless mobile liquid of specific gravity 0.623 at 0°. At — 85° it is a solid. Liquid ammonia produces a low temperature upon evaporation, and hence is used in commerce for making *artificial ice.* Ammonia is combustible with difficulty, and does not support the combustion of ordinary combustibles. Since early times ammonia has been made by distilling bones and other animal refuse.

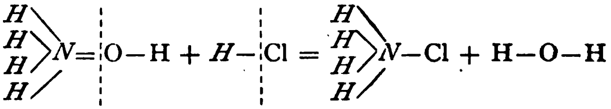
When we confine ammonia over water, the ammonia is absorbed by the water with surprising rapidity. One volume of water will at ordinary temperature hold about 700 volumes of ammonia. The saturated solution of ammonia, known as "ammonia water," at 15° contains 34.95 per cent. of the gas, and has a specific gravity of 0.882. It neutralizes acids, acting like a base in which the nitrogen and four fifths of the hydrogen constitute a positive ion. It is called *ammonium hydroxide*, and is represented by the symbol



Ammonium Salts. *From ammonia or ammonium hydroxide we may readily make the ammonium salts, in which the ammonium group is the positive ion.* When we allow gaseous ammonia, NH_3, to come in contact with gaseous hydrogen chloride, a heavy white cloud of finely divided *ammonium chloride*, NH_4Cl, is formed.



We may also get ammonium chloride by neutralizing a solution of hydrochloric acid with ammonium hydroxide, NH_4OH, and recovering the salt by evaporation.



When ammonia gas comes in contact with vapor of nitric acid, a white cloud of *ammonium nitrate*, NH_4NO_3, is formed; and the same salt may be made by neutralizing a solution of nitric acid with ammonium hydroxide.

$$NH_3 + \mathit{H}NO_3 = \mathit{NH_4}NO_3$$

$$\mathit{NH_4}OH + \mathit{H}NO_3 = \mathit{NH_4}NO_3 + H_2O$$

So also, sulphuric acid will form *ammonium sulphate*, $(NH_4)_2SO_4$, with ammonium hydroxide.

$$2\,\mathit{NH_4}OH + \mathit{H_2}SO_4 = (\mathit{NH_4})_2SO_4 + 2\,H_2O$$

With proper proportions of reacting substances *ammonium hydrogen sulphate*, NH_4HSO_4, may be formed.

$$\mathit{NH_4}\mathrm{OH} + \mathit{H}\mathrm{HSO_4} = \mathit{NH_4}\mathrm{HSO_4} + \mathrm{H_2O}$$

Carbonic acid, H_2CO_3, gives with ammonium hydroxide, NH_4OH, either *ammonium carbonate*, $(NH_4)_2CO_3$, or *ammonium hydrogen carbonate*, $(NH_4)HCO_3$, according to the proportions of the reacting substances.

$$2\,\mathit{NH_4}\mathrm{OH} + \mathit{H_2}\mathrm{CO_3} = (\mathit{NH_4})_2\mathrm{CO_3} + 2\,\mathrm{H_2O}$$

$$\mathit{NH_4}\mathrm{OH} + \mathit{H}\mathrm{HCO_3} = \mathit{NH_4}\mathrm{HCO_3} + \mathrm{H_2O}$$

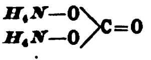
The ammonium salts are white solids, soluble in water, and easily volatilized by heating.

$H_4N{-}Cl$

Ammonium chloride, NH_4Cl, a white solid, occurs in some volcanic regions as an incrustation on the earth's surface. It is fairly soluble in water and from its solution it may be recovered in cubes or octahedra. When heated, it turns directly into a vapor without melting. At 280° it begins to dissociate into ammonia, NH_3, and hydrogen chloride, HCl, and this dissociation is complete at 350°. If the mixed gases are cooled, ammonium chloride is formed again. A similar dissociation takes place when an ammonium chloride solution is boiled.

$$\mathrm{NH_4Cl} = \mathrm{NH_3} + \mathrm{HCl}$$

Ammonium chloride is manufactured largely from the "gas liquor," formed as a by-product in the manufacture of illuminating gas, and is used in dyeing, soldering, galvanizing iron, and in charging certain kinds of electrical batteries. It was formerly obtained from organic refuse, and was called *sal ammoniac*.



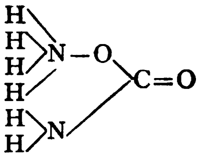
Ammonium carbonate, $(NH_4)_2CO_3$, is a soluble white solid, which readily loses ammonia at ordinary temperature, forming *ammonium hydrogen carbonate*, $(NH_4)HCO_3$.

$$\mathrm{(NH_4)_2CO_3} = \mathrm{NH_4HCO_3} + \mathrm{NH_3}$$

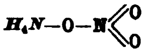
The acidic carbonate at 58° is completely decomposed into ammonia, carbon dioxide, and water.

$$\mathrm{NH_4HCO_3} = \mathrm{H_2O} + \mathrm{CO_2} + \mathrm{NH_3}$$

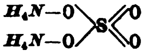
The commercial ammonium carbonate, made by fusing ammonium chloride or ammonium sulphate with calcium carbonate, consists of a mixture of ammonium hydrogen carbonate, $(NH_4)HCO_3$, and a peculiar dehydration product of the normal ammonium carbonate, known as *ammonium carbamate*,



which, however, on exposure to moist air, takes up water and becomes normal ammonium carbonate, $(NH_4)_2CO_3$.



Ammonium nitrate, NH_4NO_3, is a white crystalline, very deliquescent salt, melting easily, and readily decomposed by heating.

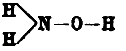


Ammonium sulphate $(NH_4)_2SO_4$, a white soluble salt, is made in large quantities from the ammonia produced in the manufacture of coal gas. It is used as a fertilizer.

"Ammonium Amalgam." When sodium amalgam, an alloy of mercury and sodium, is put into a cold saturated solution of ammonium chloride, NH_4Cl, it swells up to a soft, spongy mass, until it occupies many times its original volume. The mass evolves ammonia and hydrogen spontaneously, until nothing but mercury remains. It has been considered to be a weak and very unstable *ammonium amalgam*, a compound of the ammonium-ion with mercury.

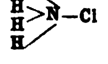
$$Hg_x \cdot Na + NH_4Cl = Hg_x \cdot NH_4 + NaCl$$

Ammonia Derivatives. *Besides ammonia there are a few other nitrogen compounds which contain hydrogen, and which, like ammonia, have basic properties, combining with acids to form salts. Hydroxylamine*, NH_2OH,



which may be formed as a product of the reduction of nitric acid, when certain metals act upon dilute nitric acid, is a colorless crystalline solid of specific gravity 1.235, melting at 33°. It is hygroscopic, and unstable at temperatures above 15°, breaking down into nitrogen, nitrogen monoxide, nitrous acid, and ammonia. The solution of hydroxylamine in water is unstable, tending to decompose into water, nitrogen, and ammonia.

$$3\,NH_2OH = 3\,H_2O + N_2 + NH_3$$

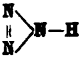


When we act upon hydroxylamine with hydrochloric acid, *hydroxylamine hydrochloride*, $NH_3(OH)Cl$, a salt, soluble in alcohol and in water, is formed.

$$NH_2OH + HCl = NH_3(OH)Cl$$

Hydroxylamine sulphate, $NH_3(OH)HSO_4$, and other similar salts may be formed from hydroxylamine.

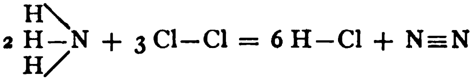
Hydrazine, N_2H_4 (diamide), formed like hydroxylamine by the reduction of the oxygen compounds of nitrogen, is a colorless fuming liquid of specific gravity 1.003. It forms with water a basic hydroxide, N_2H_5OH, which neutralizes acids, forming salts.



Hydrazoic acid, N_3H (azoimide), is a colorless mobile liquid, of strong odor, boiling at 37°, very explosive, and forming salts with bases.

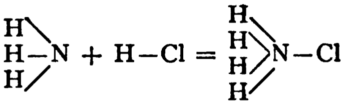
Binary Nitrogen Compounds. *Certain binary compounds of nitrogen with other elements may be made by the action of suitable reagents upon ammonia or ammonium compounds.*

When chlorine acts upon an excess of ammonia, hydrogen chloride is formed, and nitrogen is set free.



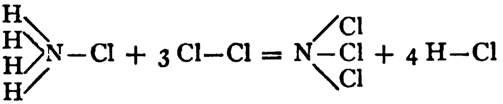
$$2\,\begin{matrix}H\diagdown\\H-N\\H\diagup\end{matrix} + 3\,Cl-Cl = 6\,H-Cl + N\equiv N$$

The hydrogen chloride, as soon as it is formed, will combine with the excess of ammonia, forming ammonium chloride.



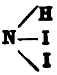
$$\begin{matrix}H\diagdown\\H-N\\H\diagup\end{matrix} + H-Cl = \begin{matrix}H\\H\\H\\H\end{matrix}\!\!>N-Cl$$

If the addition of chlorine is continued until the chlorine is in excess, the chlorine will act upon the ammonium chloride formed, with the formation of the dangerously explosive *nitrogen chloride*, NCl_3, and hydrogen chloride.

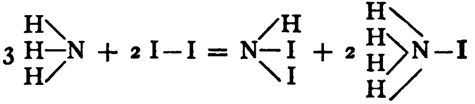


$$\begin{matrix}H\\H\\H\\H\end{matrix}\!\!>N-Cl + 3\,Cl-Cl = N\begin{matrix}\diagup Cl\\-Cl\\\diagdown Cl\end{matrix} + 4\,H-Cl$$

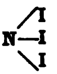
Nitrogen chloride, NCl_3, is an oily yellow liquid of specific gravity 1.65, having a characteristic odor. It decomposes with great violence when heated above 90°, or when exposed to direct sunlight, or when brought into the slightest contact with many substances. It is soluble in benzene, ether, and carbon disulphide. It is decomposed by ammonia, with the liberation of nitrogen, and by hydrochloric acid, with the liberation of chlorine, ammonium chloride being formed in each case.



Diiodoamine, NHI_2, may be formed as a dark-colored powder when ammonia is added to a solution of iodine containing potassium iodide.



$$3\,\mathrm{H_3{\equiv}N} + 2\,\mathrm{I{-}I} = \mathrm{N{\equiv}(H)(I)(I)} + 2\,\mathrm{(H)_4{>}N{-}I}$$

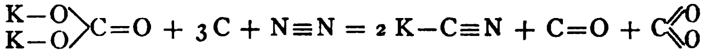


Under slightly different conditions a compound of nitrogen iodide, NI_3, and ammonia may be formed, which has the composition $NI \cdot 3\,NH_3$, which upon washing with water gives *nitrogen iodide*, NI_3. These compounds are very unstable, being readily decomposed by hydrochloric acid and by many other reagents, and when dry exploding when slightly disturbed.

Nitrogen sulphide, N_4S_4, orange-red crystals, melting at 178°, is formed by the action of sulphur dichloride, SCl_2, upon ammonia. It is explosive. *Nitrogen pentasulphide*, N_2S_5, a deep red liquid, of specific gravity 1.9, is made by the action of nitrogen sulphide, N_4S_4, upon carbon disulphide, CS_2.

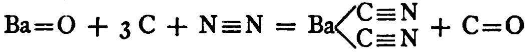
Cyanogen Compounds. *Certain compounds of nitrogen with carbon and some other element or elements are known as the cyanogen compounds.*

Cyanides. When nitrogen is passed over a heated mixture of carbon and potassium carbonate, ***potassium cyanide***, KCN, is formed.



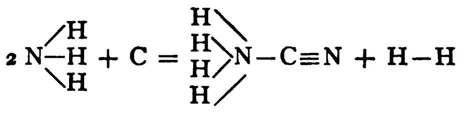
$$\mathrm{(K{-}O)_2{>}C{=}O} + 3\,\mathrm{C} + \mathrm{N{\equiv}N} = 2\,\mathrm{K{-}C{\equiv}N} + \mathrm{C{=}O} + \mathrm{C{<}^{O}_{O}}$$

Nitrogen acts similarly upon a mixture of carbon and barium oxide to form *barium cyanide*, $Ba(CN)_2$,



$$\mathrm{Ba{=}O} + 3\,\mathrm{C} + \mathrm{N{\equiv}N} = \mathrm{Ba{<}^{C\equiv N}_{C\equiv N}} + \mathrm{C{=}O}$$

and ammonia and red-hot carbon react to form ***ammonium cyanide***, NH_4CN.



$$2\,\mathrm{N{\equiv}(H)_3} + \mathrm{C} = \mathrm{(H)_4{>}N{-}C{\equiv}N} + \mathrm{H{-}H}$$

Other cyanides of the alkali metals and alkali earth metals may be produced similarly, and all are soluble in water. The soluble cyanides are very poisonous.

Hydrocyanic Acid. *By acting upon the soluble cyanides with acids, hydrogen cyanide, or hydrocyanic acid, is formed.* When we act upon potassium cyanide, KCN, with sulphuric acid, ***hydrogen cyanide***, HCN, is formed.

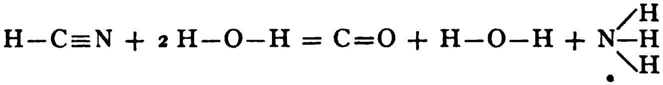
$$K{-}\mathrm{C{\equiv}N} + H{-}\mathrm{Cl} = H{-}\mathrm{C{\equiv}N} + K{-}\mathrm{Cl}$$

In the laboratory hydrogen cyanide is generally made by acting upon a complex cyanide, potassium ferrocyanide, $K_4Fe(CN)_6$, with dilute sulphuric acid.

$$2\,K_4Fe(CN)_6 + 3\,H_2SO_4 = 6\,HCN + FeK_2Fe(CN)_6 + 3\,K_2SO_4$$

Hydrogen cyanide, or *hydrocyanic acid*, HCN (prussic acid), is a mobile, intensely poisonous liquid, of specific gravity 0.697 at 18°, a crystalline solid at −15°, boiling at 26.5°, forming a colorless vapor. It is easily soluble in water, alcohol, and ether. It is inflammable, and burns with a violet flame, forming carbon dioxide, water, and nitrogen.

In the presence of concentrated acids or of alkali hydroxides in hot solution, hydrogen cyanide is hydrolyzed to formic acid, HCO_2H, which breaks up into carbon monoxide and water, with evolution of ammonia.

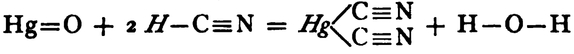


$$\mathrm{H{-}C{\equiv}N + 2\,H{-}O{-}H = C{=}O + H{-}O{-}H + N}\!\begin{array}{l}\diagup\mathrm{H}\\ -\mathrm{H}\\ \diagdown\mathrm{H}\end{array}$$

Hydrogen cyanide neutralizes basic hydroxides to form soluble cyanides, in which carbon and nitrogen constitute a negative ion. By the action of hydrogen cyanide upon potassium hydroxide, white soluble *potassium cyanide*, KCN, is obtained,

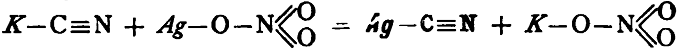
$$K{-}\mathrm{O{-}H} + H{-}\mathrm{C{\equiv}N} = K{-}\mathrm{C{\equiv}N + H{-}O{-}H}$$

while hydrogen cyanide and mercuric oxide, HgO, give white soluble *mercuric cyanide*, $Hg(CN)_2$.



$$\mathrm{Hg{=}O} + 2\,H{-}\mathrm{C{\equiv}N} = Hg\!\begin{array}{l}\diagup\mathrm{C{\equiv}N}\\ \diagdown\mathrm{C{\equiv}N}\end{array} + \mathrm{H{-}O{-}H}$$

Insoluble Cyanides. *Certain cyanides are insoluble and may be obtained as precipitates.* Potassium cyanide, KCN, and silver nitrate, $AgNO_3$, taken in proper proportions, react to form white insoluble *silver cyanide*, AgCN.



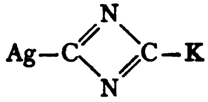
$$K{-}\mathrm{C{\equiv}N} + Ag{-}\mathrm{O{-}N}\!\begin{array}{l}\diagup\!\!\diagup\mathrm{O}\\ \diagdown\!\!\diagdown\mathrm{O}\end{array} = Ag{-}\mathrm{C{\equiv}N} + K{-}\mathrm{O{-}N}\!\begin{array}{l}\diagup\!\!\diagup\mathrm{O}\\ \diagdown\!\!\diagdown\mathrm{O}\end{array}$$

Double Cyanides. Many insoluble cyanides, like silver cyanide, are acted upon by an excess of the cyanide of an alkali element to form soluble double cyanides containing more than one positive ion. Thus, potassium cyanide, KCN, combines with silver cyanide, AgCN, to form the white soluble double cyanide, AgCN · KCN.

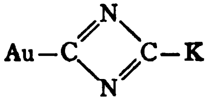
$$AgCN + KCN = AgCN \cdot KCN$$

Other similar double cyanides are AgCN · NaCN, AgCN · KCN, Au(CN) · KCN, $Hg(CN)_2 \cdot 2\,KCN$. In these double salts the constituent compounds appear to be combined loosely. When acted upon by acids, these compounds are decomposed with formation of hydrogen cyanide.

The composition of the double cyanides may be expressed in graphic form by linking together the cyanogen groups, a practice for which we find warrant in the existence of certain soluble compounds of cyanogen in polymerized form. Thus we know a *cyanogen chloride*, $CNCl$, and a polymerized form of cyanogen chloride to which we give the symbol $(CN)_3Cl_3$. The double cyanide of silver and potassium may be represented by the symbols

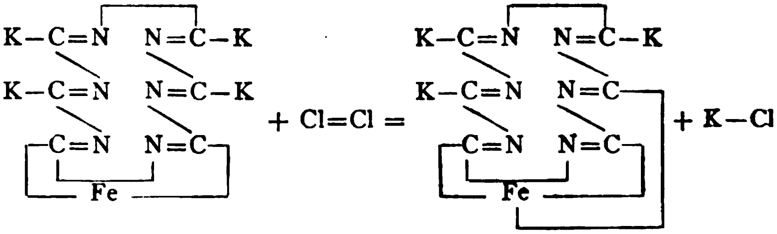


and the double cyanide of gold and potassium by the symbol



Ferro-cyanides and Ferri-cyanides. *Certain complex cyanides are more stable than the double cyanides. Potassium ferrocyanide*, $K_4Fe(CN)_6$, usually made by heating together in a retort refuse animal substances, such as blood, horn, and hair, with potassium carbonate and iron, and *potassium ferricyanide*, $K_3Fe(CN)_6$, made by treating potassium ferrocyanide with chlorine or some other oxidizing agent, are examples of such complex cyanides. These compounds, though soluble in water, when treated with an acid do not form hydrogen cyanide at once, but, on the contrary, cause the precipitation of the complex acids, *hydroferrocyanic acid*, $H_4Fe(CN)_6$, and *hydroferricyanic acid*, $H_3Fe(CN)_6$. Other complex cyanides may be formed in like manner.

The behavior of the *ferrocyanides* and the *ferricyanides*, as distinguished from that of the simple and double cyanides, may be expressed by graphic symbols in which the polymerization of the cyanogen nucleus is complex. In the following equation are shown graphic symbols for potassium ferrocyanide and potassium ferricyanide, in which the increase of valence on the part of the iron atom, which takes place when chlorine acts upon the former salt, is indicated. Other complex cyanides show similar relations.



Cyanates and Sulphocyanates. *By the oxidation of cyanides of the alkali elements, cyanates may be formed; and by the action of sulphur upon cyanides of the alkali elements, sulphocyanates may be made.* By heating potassium cyanide, KCN, with lead oxide, PbO, white soluble *potassium cyanate*, KCNO, is obtained,

$$KCN + PbO = KCNO + Pb$$

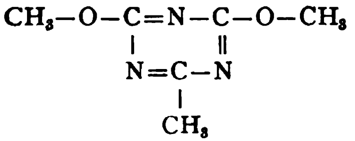
and by fusing potassium cyanide with sulphur, white soluble *potassium sulphocyanate*, KCNS, is formed.

$$KCN + S = KCNS$$

Other cyanates and sulphocyanates are known, and the corresponding *cyanic acid*, HCNO, and *sulphocyanic acid*, HCNS, as well. The formation of the blood-red *ferric sulphocyanate*, $Fe(CN)_3S_3$, furnishes a means for identifying ferric compounds in solution.

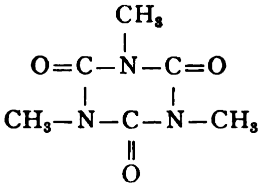
Various organic derivatives of cyanides, cyanates, and sulphocyanates possess great theoretical interest from the relations of isomerism which they present. Thus, the following symbols, representing known compounds of the radical methyl, disclose atomic relations suggested by the reactions in which these compounds take part.

$CH_3-C\equiv N$ Methyl Cyanide	$CH_3-N\equiv C$ Methyl Isocyanide
—	$CH_3-N=C=O$ Methyl Isocyanate



$$\begin{array}{c} CH_3-O-C=N-C-O-CH_3 \\ |\qquad\quad \| \\ N=C-N \\ | \\ CH_3 \end{array}$$

Methyl Cyanurate

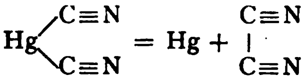


$$\begin{array}{c} CH_3 \\ | \\ O=C-N-C=O \\ |\qquad\quad | \\ CH_3-N-C-N-CH_3 \\ \| \\ O \end{array}$$

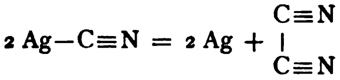
Methyl Isocyanurate

$CH_3-S-C\equiv N$ Methyl Sulphocyanate	$CH_3-N=C=S$ Methyl Isosulphocyanate

Cyanogen. *By decomposing certain cyanides, cyanogen may be obtained.* Mercuric cyanide, $Hg(CN)_2$, and silver cyanide, AgCN, when heated give the metal and a compound of carbon and nitrogen called *cyanogen*, C_2N_2, so named because several of the compounds into which it enters possess a blue color.



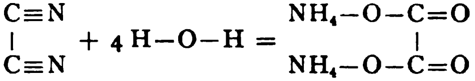
$$Hg\begin{array}{l}\diagup C\equiv N\\ \diagdown C\equiv N\end{array} = Hg + \begin{array}{c}C\equiv N\\ |\\ C\equiv N\end{array}$$



$$2\,Ag-C\equiv N = 2\,Ag + \begin{array}{c}C\equiv N\\ |\\ C\equiv N\end{array}$$

Cyanogen, C_2N_2 (dicyanogen), which may also be produced in other ways, is a colorless gas, condensing to a mobile liquid at −25°, or under a pressure of 5 atmospheres, having a specific gravity of 0.866; solidifying at −34° to a crystalline mass; boiling at −21°. Cyanogen gas is very poisonous, and has a peculiar odor suggesting the odor of peach stones. It is soluble in water and alcohol. It burns with a bluish purple flame, forming carbon dioxide and nitrogen.

The water solution of cyanogen undergoes spontaneous hydrolysis, with formation of ammonium oxalate, and this reaction is hastened by presence of an acid.



$$\begin{array}{c}C\equiv N\\ |\\ C\equiv N\end{array} + 4\,H-O-H = \begin{array}{r}NH_4-O-C=O\\ |\\ NH_4-O-C=O\end{array}$$

A polymeric form of cyanogen, $(CN)_n$, of unknown molecular weight, remains in solid form when cyanogen is evolved at moderate heat from mercuric cyanide. It is resolved into dicyanogen, $(CN)_2$, at a higher temperature.

Preparation of Nitrogen. *We have seen that many of the nitrogen compounds may be decomposed, with the liberation of nitrogen. Several of these reactions of decomposition may be utilized for the preparation of pure nitrogen.*

When a mixture of ammonium nitrate, NH_4NO_3, and ammonium chloride, NH_4Cl, is heated, water is formed, and a mixture of nitrogen and chlorine is evolved, from which the chlorine may be separated by passing through a solution of sodium hydroxide or calcium hydroxide.

$$4\,NH_4NO_3 + 2\,NH_4Cl = 12\,H_2O + Cl_2 + 5\,N_2$$

When ammonium nitrite, NH_4NO_2, is heated, water is formed, and nitrogen is set free.

$$NH_4NO_2 = 2\,H_2O + N_2$$

In practice a similar result may be obtained by warming a solution of equal parts of ammonium chloride, NH_4Cl, and sodium nitrite, $NaNO_2$, in an equal volume of water.

$$NH_4Cl + NaNO_2 = NaCl + 2\,H_2O + N_2$$

When ammonium dichromate, $(NH_4)_2Cr_2O_7$, is heated, chromium trioxide, Cr_2O_3, and water are formed, and nitrogen is evolved.

$$(NH_4)_2Cr_2O_7 = Cr_2O_3 + 4\,H_2O + N_2$$

In practice it is best to heat a mixture of ammonium chloride, NH_4Cl, and potassium dichromate, $K_2Cr_2O_7$, with a similar result.

$$2\,NH_4Cl + K_2Cr_2O_7 = Cr_2O_3 + 2\,KCl + 4\,H_2O + N_2$$

When chlorine gas is passed through a solution of ammonia, NH_3, care being taken to keep the ammonia in excess, to prevent the possible formation of nitrogen chloride, the ammonia is completely reduced with formation of hydrogen chloride, and evolution of nitrogen.

$$2\,NH_3 + 3\,Cl_2 = 6\,HCl + N_2$$

In practice a stream of chlorine is passed from the chlorine generator through a concentrated ammonia solution contained in a flask from which the evolved nitrogen may be collected over water in a pneumatic trough.

Summary. *We note two distinct classes of nitrogen compounds — the nitrogen oxides, and their derivatives, the nitrogen acids and their salts; and ammonia, and its derivatives, the ammonium compounds.*

The nitrogen oxides may be prepared by decomposing nitric acid or nitrates. Nitric acid is a colorless liquid, readily neutralizing bases, forming nitrates generally soluble in water, in which nitrogen is a constituent of the negative ion. It is decomposed by heating. Nitric acid is acted upon by many positive elements with the formation of nitrates, and nitrogen oxides, nitrogen, ammonia, or other reduction products containing nitrogen. Nitrates may be decomposed by heating with the formation of nitrites or nitrogen oxides and other products.

Nitrous acid exists in solution only; its salts, the nitrites, in which nitrogen is in the negative ion, may be decomposed by acids with the formation of nitrogen oxides. Sodium nitrite and potassium nitrite are soluble in water. Hyponitrites and hyponitrous acid may be made by reducing nitrites.

Ammonia is a colorless gas, forming with water ammonium hydroxide, which acts like a basic hydroxide, in which nitrogen and four fifths of the hydrogen constitute a positive ion. Both ammonia and ammonium hydroxide form with acids ammonium salts, easily soluble, volatilized by heat, and decomposed by bases with the liberation of ammonia.

Hydroxylamine, hydrazine, and hydrazoic acid, like ammonia, contain nitrogen and hydrogen, and form salts. By the action of chlorine upon ammonia or ammonium compounds, nitrogen chloride may be formed, and nitrogen compounds of iodine and of sulphur may also be formed from ammonium compounds. Cyanogen, composed of carbon and nitrogen, exists by itself and as a negative ion in combination with many elements in cyanides, both simple and complex.

Nitrogen may be liberated from some of its compounds containing both oxygen and hydrogen and from others by the action of suitable reagents.

Phosphorus, P, 31.0

Native Phosphates. The most abundant native compounds of phosphorus are the *phosphates*, salts of orthophosphoric acid, H_3PO_4. The mineral *phosphorite*, the most important naturally occurring phosphate, consists of the insoluble calcium orthophosphate, $Ca_3(PO_4)_2$, combined with fluorine or chlorine. By the weathering of phosphatic rocks, the phosphates pass into the soil, where they constitute an important source of plant food. In animal bodies phosphates are present in some fluid secretions, but principally in the bones, the solid matter of which consists principally of calcium orthophosphate. When the organic matter of bones is removed by burning or by treatment with superheated steam, nearly pure calcium orthophosphate remains. Other phosphates may be recovered from *guano* and other animal products.

Phosphorus. *Phosphorus* is usually prepared by heating tricalcium orthophosphate, $Ca_3(PO_4)_2$ (*bone phosphate*), with silicon dioxide and carbon, or with sulphuric acid; or by heating the acidic phosphate, $CaH_4(PO_4)_2$, or phosphoric acid, H_3PO_4, with carbon, the phosphorus vapor being collected and solidified under water. The impure phosphorus thus obtained is purified by melting under warm water, and straining, or by redistilling, after which it is cast into sticks for use.

Allotropic Forms of Phosphorus. *Phosphorus* exists in three *allotropic modifications*, yellow phosphorus, red phosphorus, and a third more crystalline and denser variety. The common *yellow phosphorus*, when first prepared, is a nearly colorless, transparent, soft, waxy solid, which upon exposure to sunlight turns yellow, becoming finally reddish and non-transparent on the surface. It has a specific gravity of 1.83 at 10°. Under water it melts at 44.4°, and boils at 287°. The specific gravity and molecular weight of phosphorus vapor is 124, corresponding to the molecular symbol P_4. Yellow phosphorus is soft and tough at ordinary temperatures, but is brittle at 0°. It is insoluble in water, slightly soluble in alcohol and ether, but very readily soluble in carbon disulphide, from which solution it may be recovered in crystals. Yellow phosphorus is very active chemically, oxidizing spontaneously at ordinary temperatures, and inflaming when slightly warmed. A piece of paper, or cotton fiber, moistened with a carbon disulphide solution of phosphorus, will be set on fire spontaneously by the inflaming phosphorus, as soon as the carbon disulphide has evaporated. In the dark, yellow phosphorus exhibits a characteristic glowing or *phosphorescence*, caused by the slow formation of a compound of phosphorus and hydrogen. Yellow phosphorus is very poisonous, causing a peculiar disease of the bones.

Red phosphorus is a reddish brown powder, of specific gravity 2.19, minutely crystalline in form. It does not melt, even at red heat, and it vaporizes slowly under 100°. It is insoluble in water and in carbon disulphide. It is very stable, remaining unaltered in dry air, and exhibiting no phosphorescence. It inflames at 260°. Red phosphorus is prepared by heating yellow phosphorus to 300° in closed vessels free from air, cooling, and extracting the unchanged yellow phosphorus with carbon disulphide. When the red phosphorus is heated above 260° in an inert atmosphere, it forms vapors which, when condensed quickly, produce the ordinary yellow phosphorus. Red phosphorus is not poisonous.

When yellow phosphorus is heated in a closed tube, free from air, to 530°, or when yellow phosphorus is heated with lead to redness, it forms small black shining crystals, of specific gravity 2.34, vaporizing with difficulty, and having a metallic appearance.

Phosphorus, especially the yellow phosphorus, is very active chemically, combining energetically with oxygen, hydrogen, chlorine, and similar elements, and with many metals, forming compounds which we shall study in order.

Oxides and Hydroxides.

The phosphorus oxides are two in number, holding different amounts of oxygen, while there are several phosphorus hydroxides, some of which may be formed from known corresponding phosphorus oxides. Thus we have:

OXIDES	HYDROXIDES
Phosphorus pentoxide, P_2O_5	Orthophosphoric acid, H_3PO_4
——	Pyrophosphoric acid, $H_4P_2O_7$
——	Metaphosphoric acid, HPO_3
Phosphorus trioxide, P_2O_3 and P_4O_6	Phosphorous acid, H_3PO_3
——	Hypophosphoric acid, $H_4P_2O_6$
——	Hypophosphorous acid, H_3PO_2

Orthophosphoric acid, H_3PO_4, may be formed from the phosphorus pentoxide, P_2O_5, and corresponds to that oxide; phosphorous acid, H_3PO_3, corresponds to the ideal phosphorus trioxide, P_2O_3, which, however, in a state of vapor, has the polymerized composition, P_4O_6. Phosphorous acid may be made from this oxide. Phosphorus pentoxide and phosphorus trioxide are therefore the anhydrides of orthophosphoric acid and phosphorous acid respectively. Pyrophosphoric acid, $H_4P_2O_7$, and metaphosphoric acid, HPO_3, are oxyhydroxides, being anhydrides formed by removing the elements of water from orthophosphoric acid. Hypophosphoric acid, $H_4P_2O_6$, is intermediate between orthophosphoric acid and phosphorous acid, being formed when phosphorus is slowly oxidized in presence of water. Hypophosphorous acid, H_3PO_2, contains less oxygen than phosphorous acid, and resembles both a hydroxide and a hydride. The phosphorus hydroxides may all be formed when phosphorus is allowed to slowly oxidize spontaneously in moist air.

Phosphorus Oxides.

We may prepare the two phosphorus oxides by oxidizing phosphorus directly.

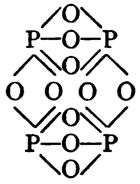
Phosphorus pentoxide, P_2O_5, is formed when phosphorus is burned in an excess of oxygen or dry air.

$$4\,P + 5\,O_2 = 2\,P_2O_5$$

The possible constitution of phosphorus pentoxide may be made a matter of discussion. If we assign to phosphorus the symbol

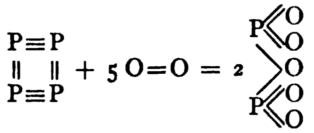
$$\begin{array}{c} P\equiv P \\ \|\quad\ \| \\ P\equiv P \end{array}$$

suggested by the specific gravity of phosphorus in vapor condition, we might conceive phosphorus pentoxide, formed by the complete oxidation of phosphorus, to have a similar constitution



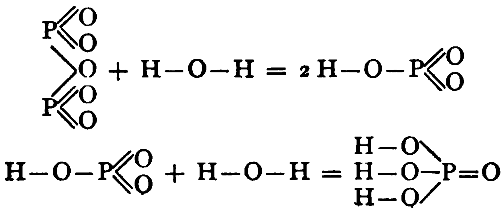
Of the molecular weight of phosphorus in solid condition, or of phosphorus pentoxide, however, we have no knowledge, so we find it convenient to represent both substances by the simplest possible equivalent symbols, P and P_2O_5.

The formation of phosphorus pentoxide may be represented graphically by the equation:



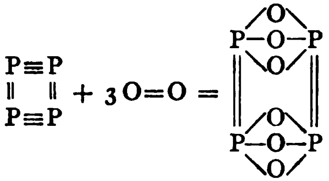
Phosphorus pentoxide may be prepared in quantity by igniting pieces of phosphorus contained in an iron dish suitably placed within a vessel into which dry oxygen or air is drawn by means of an aspirator. Phosphorus pentoxide is a voluminous white flocculent powder, slightly volatile at extremely high temperatures, very hygroscopic and deliquescent in ordinary air. It is largely employed as a desiccator or drying agent.

Phosphorus pentoxide combines with water with great evolution of heat, forming a solution of *metaphosphoric acid*, HPO_3, from which, after boiling, *orthophosphoric acid*, H_3PO_4, may be obtained. Phosphorus pentoxide is the anhydride of the phosphoric acids.

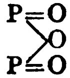


Phosphorus trioxide, P_4O_6, may be formed by gently heating phosphorus in a tube, through which is passed a stream of dry oxygen or air. Phosphorus trioxide exists either as colorless needles or as a white flocculent solid, of specific gravity 1.9, melting at 22.5°, subliming readily. The specific gravity of its vapor is 224, showing that in vapor form it has the composition shown by the symbol P_4O_6. It decomposes at 400°, yielding phosphorus, and when exposed to oxygen or air it quickly oxidizes to phosphorus pentoxide.

Since we know that the molecular weight of phosphorus trioxide, P_4O_6, corresponds to the molecular condition of phosphorus, P_4, we may represent the formation of phosphorus trioxide by the equation:



We shall find it more convenient, however, as in the case of phosphorus pentoxide, to represent phosphorus trioxide by its simplest symbol,

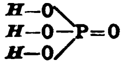


Phosphorus trioxide slowly combines with cold water, forming *phosphorous acid*, H_3PO_3, of which it is the anhydride.

$$P_2O_3 + 3\,H_2O = 2\,H_3PO_3$$

When hot water is used, the reaction is much more complex, *orthophosphoric acid*, H_3PO_4, and other products being formed. The constitution of phosphorous acid we shall discuss later.

Phosphoric Acids. *In studying the phosphorus hydroxides we commence with orthophosphoric acid and the oxyacids derived from it which may be obtained from the corresponding phosphorus pentoxide.*

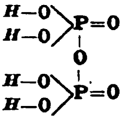


When an excess of dilute sulphuric acid acts upon calcium orthophosphate, $Ca_3(PO_4)_2$, *orthophosphoric acid*, H_3PO_4, and calcium sulphate are formed.

$$Ca_3(PO_4)_2 + 3\,H_2SO_4 = 2\,H_3PO_4 + 3\,CaSO_4$$

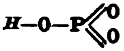
From the resulting concentrated solution the nearly insoluble calcium sulphate may be removed by filtration, and the excess of sulphuric acid and water may be removed by evaporation, leaving a residue which, boiled with water, yields the orthophosphoric acid as a thick colorless sirup. From this slightly impure phosphoric acid, upon standing, colorless prismatic crystals may be deposited, which melt at 38.6°, are very hygroscopic, and rapidly turn into a sirupy liquid when exposed to damp air.

The normal orthophosphoric acid evolves water when heated, forming pyrophosphoric acid and metaphosphoric acid, oxyacids containing higher proportions of phosphorus and oxygen, and smaller proportions of water, than are present in the orthophosphoric acid. When orthophosphoric acid, H_3PO_4, is heated to 260°, each two equivalents of it lose one equivalent of water, becoming thereby converted into *pyrophosphoric acid,* $H_4P_2O_7$ (diphosphoric acid), a white, opaque, crystalline solid, soluble in water.



$$2\ H_3PO_4 = H_4P_2O_7 + H_2O$$

When the temperature is raised to 300°, each equivalent of the orthophosphoric acid loses one equivalent of water, forming *metaphosphoric acid,* HPO_3, a transparent glassy mass, soluble in water and deliquescent.



$$H_3PO_4 = HPO_3 + H_2O$$

At 300° pyrophosphoric acid is similarly decomposed, forming metaphosphoric acid.

$$H_4P_2O_7 = 2\ HPO_3 + H_2O$$

Metaphosphoric acid, HPO_3, combines with water with a rapidity increasing with the temperature, forming orthophosphoric acid,

$$HPO_3 + H_2O = H_3PO_4$$

and pyrophosphoric acid, $H_4P_2O_7$, acts in a similar manner.

$$H_4P_2O_7 + H_2O = 2\ H_3PO_4$$

Interaction of Phosphoric Acids with Bases.

The phosphoric acids are strong acids and readily neutralize bases, with the formation of water and phosphates, — salts in which phosphorus is in the negative ion.

By the action of orthophosphoric acid upon bases the orthophosphates may be formed; and since orthophosphoric acid is tribasic, we may have both neutral and acidic orthophosphates.

The monacidic sodium hydroxide forms with orthophosphoric acid three kinds of salts — one neutral orthophosphate and two acidic orthophosphates. When we act upon sodium hydroxide with orthophosphoric acid, H_3PO_4, in such proportions that three equivalents of the base act upon one equivalent of the acid, neutral *trisodium orthophosphate*, Na_3PO_4, is formed.

$$3\,\mathit{Na}OH + \mathit{H}_3PO_4 = \mathit{Na}_3PO_4 + 3\,H_2O$$

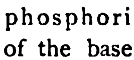
When two equivalents of sodium hydroxide act upon one equivalent of orthophosphoric acid, *disodium hydrogen orthophosphate*, Na_2HPO_4, is formed,

$$2\,\mathit{Na}OH + \mathit{H}_2HPO_4 = \mathit{Na}_2HPO_4 + 2\,H_2O$$

while the action of one third the full equivalent quantity of sodium hydroxide will give *sodium dihydrogen orthophosphate.*

$$\mathit{Na}OH + \mathit{H}H_2PO_4 = \mathit{Na}H_2PO_4 + H_2O$$

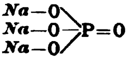
Sodium Phosphates.



The sodium orthophosphates are white solids, readily soluble in water, recoverable from solution as crystals containing water of crystallization which may be removed by heating. The most important of the three salts, *disodium hydrogen orthophosphate*, Na_2HPO_4, is formed by neutralizing orthophosphoric acid with sodium hydroxide, added until litmus shows a feebly alkaline reaction, or, with sodium carbonate, Na_2CO_3, added until effervescence ceases.

$$\mathit{Na}_2CO_3 + \mathit{H}_2HPO_4 = \mathit{Na}_2HPO_4 + H_2O + CO_2$$

From the solution the acidic orthophosphate may be recovered by evaporation at the ordinary temperature as crystals having the composition $Na_2HPO_4 \cdot 12\,H_2O$. This salt is the common "sodium phosphate."



The neutral *trisodium orthophosphate*, Na_3PO_4, is usually prepared by adding sodium hydroxide in proper excess to disodium hydrogen orthophosphate, Na_2HPO_4. It may be recovered from solution as prismatic crystals having the composition $Na_3PO_4 \cdot 12\,H_2O$, which lose eleven molecules of water at 100° and all of their water at red heat.

$$\mathit{Na}OH + \mathit{Na}_2\mathit{H}PO_4 = \mathit{Na}_3PO_4 + H_2O$$

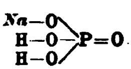
Trisodium orthophosphate may also be obtained in anhydrous condition by fusing the disodium hydrogen orthophosphate with an excess of sodium carbonate.

$$Na_2CO_3 + 2\,Na_2HPO_4 = 2\,Na_3PO_4 + H_2O + CO_2$$

The trisodium orthophosphate, however, is quite unstable, somewhat hydrolyzed in solution, and attacked by even so weak an acid as carbonic acid, with the formation of disodium hydrogen orthophosphate.

$$Na_3PO_4 + H_2O = Na_2HPO_4 + NaOH$$

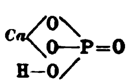
$$2\,Na_3PO_4 + CO_2 + H_2O = 2\,Na_2HPO_4 + Na_2CO_3$$

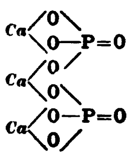


Sodium dihydrogen orthophosphate, NaH_2PO_4, is usually prepared by acting upon disodium hydrogen orthophosphate, Na_2HPO_4, with orthophosphoric acid, H_3PO_4. It may be recovered from solution in crystals having the composition $NaH_2PO_4 \cdot H_2O$, which lose their water of crystallization at 100°.

Potassium hydroxide forms with orthophosphoric acid three classes of orthophosphates, similar to the sodium orthophosphates, and similar salts of the other alkali elements may also be formed. The orthophosphates of the alkali elements are all soluble in water.

Insoluble Orthophosphates. *The orthophosphates of many elements are insoluble and may be produced as characteristic precipitates.*





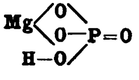
By acting upon a solution of an orthophosphate, not too acidic, such as disodium hydrogen phosphate, Na_2HPO_4, with a solution of a soluble salt of calcium, such as calcium chloride, $CaCl_2$, we may obtain a precipitate of white *calcium hydrogen orthophosphate*, $CaHPO_4$, or of *tricalcium orthophosphate*, $Ca_3(PO_4)_2$, according to the conditions and the proportions in which the substances interact.

$$Na_2HPO_4 + CaCl_2 = \mathbf{CaHPO_4} + 2\,NaCl$$

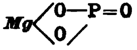
$$4\,Na_2HPO_4 + 3\,CaCl_2 = \mathbf{Ca_3(PO_4)_2} + 2\,NaH_2PO_4 + 6\,NaCl$$

Both these precipitates are acted upon by dilute acids with formation of an acidic calcium phosphate, or of phosphoric acid, according to conditions. When neutral calcium orthophosphate, $Ca_3(PO_4)_2$, is acted upon by the proper amount of sulphuric acid, the soluble acidic phosphate $CaH_4O_6(PO)_2$ is formed. This is the so-called *superphosphate*, made by acting upon phosphatic rock or upon bone ash with sulphuric acid, and employed as a fertilizer.

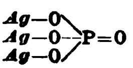
$$Ca_3(PO_4)_2 + 2\,H_2SO_4 = CaH_4O_8(PO)_2 + 2\,CaSO_4$$



By adding a soluble salt of magnesium, such as magnesium sulphate, $MgSO_4$, to a solution of disodium hydrogen orthophosphate, a white fairly insoluble precipitate of *magnesium hydrogen orthophosphate*, $MgHPO_4$, or the more insoluble *trimagnesium orthophosphate*, $Mg_3(PO_4)_2$, may be obtained, both of which are similar to the corresponding calcium salts. In the presence of ammonium hydroxide, NH_4OH, and of an ammonium salt, such as ammonium chloride, NH_4Cl, the precipitate consists of the white *ammonium magnesium orthophosphate*, NH_4MgPO_4. If the precipitation is effected slowly, best by adding ammonium hydroxide very slowly to the solution of the magnesium salt and the orthophosphate, the precipitate is crystalline. It is acted upon by dilute acids.



$$Na_2HPO_4 + NH_4OH + MgSO_4 = \mathbf{NH_4MgPO_4} + Na_2SO_4 + H_2O$$

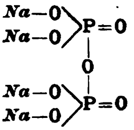


A soluble silver salt, such as silver nitrate, $AgNO_3$, precipitates in solutions of disodium hydrogen orthophosphate, yellow *silver orthophosphate*, Ag_3PO_4, acted upon by nitric acid and by ammonium hydroxide.

$$Na_2HPO_4 + 3\,AgNO_3 = \mathbf{Ag_3PO_4} + 2\,NaNO_3 + HNO_3$$

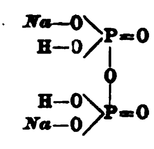
When to a solution of disodium hydrogen orthophosphate acidified with nitric acid, ammonium molybdate, $(NH_4)_2MoO_4$, is added, a pale yellow precipitate of *ammonium phosphomolybdate* forms, to which the composition $(NH_4)_3PO_4 \cdot 11\,MoO_3 \cdot 6\,H_2O$ is assigned.

Oxysalts. *The acidic sodium orthophosphates, like orthophosphoric acid, may be decomposed by heat, with evolution of water and the formation of sodium pyrophosphate and sodium metaphosphate.*



When disodium hydrogen orthophosphate, Na_2HPO_4, is heated to 300°, each two equivalents of it evolve one equivalent of water, and neutral *sodium pyrophosphate*, $Na_4P_2O_7$ (sodium diphosphate), is formed as a colorless glassy mass, soluble in water. From its solution in water, it may be recovered as prismatic crystals, $Na_4P_2O_7 \cdot 10\,H_2O$.

$$2\,Na_2HPO_4 = Na_4P_2O_7 + H_2O$$

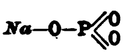


When the disodium hydrogen orthophosphate is heated to 150° with concentrated hydrochloric acid, every two equivalents of it lose one equivalent of water, while at the same time half of the sodium is replaced by hydrogen, with formation of the acidic *disodium dihydrogen pyrophosphate*, $Na_2H_2P_2O_7$ (disodium dihydrogen diphosphate), a white solid soluble in water.

$$2\,Na_2HPO_4 + 2\,HCl = Na_2H_2P_2O_7 + H_2O + 2\,NaCl$$

The same compound may be produced by heating sodium dihydrogen orthophosphate to about 200°, when each two equivalents of it lose one equivalent of water.

$$2\,NaH_2PO_4 = Na_2H_2P_2O_7 + H_2O$$



When a solution of sodium dihydrogen orthophosphate is heated to 240°, each equivalent of it loses one equivalent of water, and *sodium metaphosphate*, $NaPO_3$, is formed as a soluble white solid.

$$NaH_2PO_4 = NaPO_3 + H_2O$$

The sodium metaphosphate may also be obtained by heating the disodium dihydrogen pyrophosphate, $Na_2H_2P_2O_7$, to 240°, when each equivalent of it loses one equivalent of water.

$$Na_2H_2P_2O_7 = 2\,NaPO_3 + H_2O$$

Instead of the simple sodium metaphosphate, $NaPO_3$, several polymeric modifications, represented above, of the same compound, such as $Na_2P_2O_6$, $Na_3P_3O_9$, and $Na_6P_6O_{18}$, may be obtained when the orthophosphates or pyrophosphates are heated. These metaphosphates, formed as glassy residues when the sodium dihydrogen orthophosphate is heated, are turned to account in analytical work, — since they tend, when heated, to form pyrophosphates and orthophosphates, and in so doing will absorb some oxides of metals with the formation of complex phosphates of characteristic colors. In making such tests the sodium phosphate is fused into a transparent bead in a loop of platinum wire, and the bead is then dipped into the powdered oxide, and again fused in a blowpipe flame until the oxide or the reduced metal becomes thoroughly incorporated into the glass, and the bead assumes a characteristic color.

Sodium tetraphosphate, $Na_6P_4O_{13}$, resembling sodium pyrophosphate, $Na_4P_2O_7$, has been obtained by fusing sodium orthophosphate or sodium pyrophosphate with polymerized sodium metaphosphate. A similar insoluble *silver tetraphosphate*, $Ag_6P_4O_{13}$, may be obtained. Very many other complex phosphates have been prepared.

Interaction of Oxyphosphoric Acids with Bases. *Sodium pyrophosphate and sodium metaphosphate may also be formed by the neutralization of pyrophosphoric acid and metaphosphoric acid respectively by sodium hydroxide.* When we act upon a solution of pyrophosphoric acid, $H_4P_2O_7$, with sodium hydroxide, in such proportions that one equivalent of the acid will be neutralized by four equivalents of the base, we may obtain *sodium pyrophosphate*, $Na_4P_2O_7$,

$$4\,\mathit{Na}\mathrm{OH} + \mathit{H}_4\mathrm{P_2O_7} = \mathit{Na}_4\mathrm{P_2O_7} + 4\,\mathrm{H_2O}$$

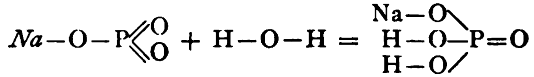
and with one half as much sodium hydroxide, *disodium dihydrogen pyrophosphate*, $Na_2H_2P_2O_7$, is formed.

$$2\,\mathit{Na}\mathrm{OH} + \mathit{H}_2\mathrm{H_2P_2O_7} = \mathit{Na}_2\mathrm{H_2P_2O_7} + 2\,\mathrm{H_2O}$$

When we act upon metaphosphoric acid, HPO_3, with an excess of sodium hydroxide, *sodium metaphosphate*, $NaPO_3$, or one of its polymeric modifications, may be obtained.

$$\mathit{Na}\mathrm{OH} + \mathit{H}\mathrm{PO_3} = \mathit{Na}\mathrm{PO_3} + \mathrm{H_2O}$$

Hydration of Oxysalts. *The sodium metaphosphates and the sodium pyrophosphates may be changed into sodium orthophosphate by the action of water or of other reagents.* When a water solution of sodium metaphosphate, $NaPO_3$, or of one of its polymeric modifications, is warmed, sodium dihydrogen orthophosphate, NaH_2PO_4, is gradually formed.



$$\mathit{Na}\mathrm{-O-P}\!\begin{smallmatrix}\nearrow \mathrm{O}\\ \searrow \mathrm{O}\end{smallmatrix} + \mathrm{H-O-H} = \begin{matrix}\mathrm{Na-O}\diagdown\\ \mathrm{H-O-P{=}O}\\ \mathrm{H-O}\diagup\end{matrix}$$

The same compound may be formed by warming sodium metaphosphate with nitric acid, or by fusing it with sodium hydroxide.

A water solution of sodium pyrophosphate, $Na_4P_2O_7$, remains unchanged when warmed, but when such a solution is heated with a dilute acid, such as nitric acid, it becomes rapidly changed into sodium dihydrogen orthophosphate, NaH_2PO_4.

$$\mathrm{Na_4P_2O_7} + \mathrm{H_2O} + 2\,\mathrm{HNO_3} = 2\,\mathrm{NaH_2PO_4} + 2\,\mathrm{NaNO_3}$$

The change of a pyrophosphate to an orthophosphate may be also effected by fusing the pyrophosphate with sodium hydroxide.

Soluble pyrophosphates and metaphosphates of potassium, and of the other alkali elements, may be produced by the decomposition of the corresponding orthophosphates, or by the neutralization of pyrophosphoric acid by alkali hydroxides.

Insoluble Oxysalts. *Some pyrophosphates and metaphosphates, like the orthophosphates, are insoluble and may be precipitated by adding reagents to solutions of pyrophosphoric acid or pyrophosphates, or metaphosphoric acid, or metaphosphates.* By adding silver nitrate, $AgNO_3$, to a solution of a soluble pyrophosphate, such as sodium pyrophosphate, $Na_4P_2O_7$, a precipitate of white crystalline *silver pyrophosphate*, $Ag_4P_2O_7$, may be obtained.

$$Na_4P_2O_7 + 4\,AgNO_3 = \mathbf{Ag_4P_2O_7} + 4\,NaNO_3$$

By adding silver nitrate to a solution of a soluble metaphosphate, such as sodium metaphosphate, $NaPO_3$, or some polymerized form of it, we may get a precipitate of white *silver metaphosphate*, $AgPO_3$, acted upon by an excess of either reagent.

$$NaPO_3 + AgNO_3 = \mathbf{AgPO_3} + NaNO_3$$

Ammonium Orthophosphates. *The ammonium orthophosphates, formed by the neutralization of orthophosphoric acid with ammonium hydroxide, are similar to the sodium orthophosphates.* By neutralizing orthophosphoric acid, H_3PO_4, with ammonium hydroxide, we may obtain either *diammonium hydrogen orthophosphate* $(NH_4)_2HPO_4$, or *ammonium dihydrogen orthophosphate*, $(NH_4)H_2PO_4$, or *triammonium orthophosphate* $(NH_4)_3PO_4$, according to the proportions in which the base and the acid react. All three salts may be recovered from solution as hydrous prismatic crystals.

Microcosmic Salt. *Sodium ammonium hydrogen orthophosphate*, the so-called "microcosmic salt," $Na(NH_4)HPO_4$, may be prepared by adding ammonium chloride to a concentrated solution of disodium hydrogen orthophosphate, Na_2HPO_4, and may be recovered from the solution as colorless prismatic crystals.

$$Na_2HPO_4 + NH_4Cl = Na(NH_4)HPO_4 + NaCl$$

The salt is readily decomposed by heating, with the evolution of ammonia, and formation of sodium dihydrogen orthophosphate, NaH_2PO_4, which, upon further heating, evolves water, leaving a mass of polymerized sodium metaphosphate, which first forms a colorless liquid, and then hardens into a clear glass.

Phosphorous Acid. *Phosphorous acid*, H_3PO_3, which, as we have seen, may be made by the action of cold water upon phosphorus trioxide, P_4O_6, is best prepared by the action of water upon phosphorus trichloride, PCl_3, a compound of phosphorus which we shall study later.

$$PCl_3 + 3\ H_2O = H_3PO_3 + 3\ HCl$$

By evaporating the resulting solution a thick sirupy liquid is obtained, from which, by evaporation in a vacuum, the phosphorous acid separates as colorless crystals, which melt at 70°, are readily soluble in water, and are hygroscopic, deliquescing rapidly in the air.

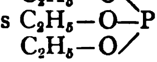
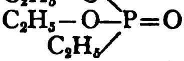
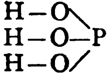
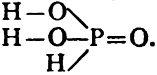
When heated, phosphorous acid is decomposed with formation of orthophosphoric acid and phosphorus trihydride.

$$4\ H_3PO_3 = 3\ H_3PO_4 + PH_3$$

Constitution of Phosphorous Acid. When phosphorous acid is acted upon by sodium hydroxide, two products of neutralization are formed, having the composition NaH_2PO_3 and Na_2HPO_3.

$$NaOH + H_3PO_3 = NaH_2PO_3 + H_2O$$

$$2\ NaOH + H_3PO_3 = Na_2HPO_3 + 2\ H_2O$$

One third of the hydrogen of phosphorous acid appears not to be replaced by the action of the equivalent amount of sodium hydroxide. So it is obvious that we must either suppose one third of the hydrogen to be replaced with extreme difficulty, or else we must regard phosphorous acid as actually a dibasic acid, in which one third of the hydrogen is peculiarly related in the compound. Some light is thrown upon this relation by a study of certain organic compounds containing organic radicals, oxygen and phosphorus. Two such compounds, differing in properties, but having exactly the same composition, $(C_2H_5)_3PO_3$, have been recognized, and have been distinguished from each other by assigning to them the constitutions represented by the graphic symbols  $\begin{array}{l}C_2H_5-O\diagdown\\C_2H_5-O-P\\C_2H_5-O\diagup\end{array}$ and  $\begin{array}{l}C_2H_5-O\diagdown\\C_2H_5-O-P=O\\C_2H_5\diagup\end{array}$ respectively. The hydroxides, corresponding to these two compounds respectively, would have the symbols  $\begin{array}{l}H-O\diagdown\\H-O-P\\H-O\diagup\end{array}$ and  $\begin{array}{l}H-O\diagdown\\H-O-P=O\\H\diagup\end{array}$. It is possible that both these phosphorous acids may exist, but since ordinary phosphorous acid behaves like a dibasic acid, it is customary to regard the second symbol as representing at least the more stable form of phosphorous acid, and to employ it in representing the formation of salts by the interaction of phosphorous acid with bases.

Phosphites. *By the neutralization of phosphorous acid with bases, we may get the phosphites.* Sodium hydroxide acts upon phosphorous acid, H_3PO_3, to form *sodium phosphite*, Na_2HPO_3,

$$2\,\mathit{Na}OH + \mathit{H_2}HPO_3 = \mathit{Na_2}HPO_3 + 2\,H_2O$$

or *sodium hydrogen phosphite*, NaH_2PO_3,

$$\mathit{Na}OH + \mathit{H}H_2PO_3 = \mathit{Na}H_2PO_3 + H_2O$$

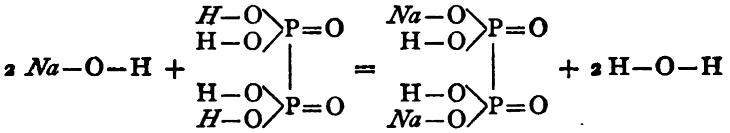
according to the proportions in which the substances react. These salts are white soluble solids. Similar soluble and insoluble phosphites of other elements are known.

Phosphorous acid is changed into phosphoric acid by atmospheric oxygen and by other oxidizing agents.

$$2\,H_3PO_3 + O_2 = 2\,H_3PO_4$$

The phosphites are not readily affected by oxygen, but may be oxidized by strong oxidizers, and are able to reduce salts of mercury and silver, setting the metals free.

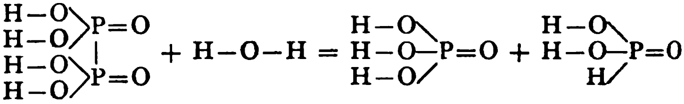
Hypophosphoric Acid and Hypophosphates. *Hypophosphoric acid*, $H_4P_2O_6$, is formed along with orthophosphoric acid and phosphorous acid when phosphorus is allowed to oxidize slowly in a limited supply of moist air. By adding sodium hydroxide to the mixture of the three acids thus formed, the difficultly soluble acidic salt, *disodium dihydrogen hypophosphate*, $Na_2H_2P_2O_6$, separates out.



$$2\,\mathit{Na}-O-H + \begin{array}{c} \left.\begin{array}{l}\mathit{H}-O\\ H-O\end{array}\right\rangle P=O \\ \quad | \\ \left.\begin{array}{l}H-O\\ \mathit{H}-O\end{array}\right\rangle P=O \end{array} = \begin{array}{c} \left.\begin{array}{l}\mathit{Na}-O\\ H-O\end{array}\right\rangle P=O \\ \quad | \\ \left.\begin{array}{l}H-O\\ \mathit{Na}-O\end{array}\right\rangle P=O \end{array} + 2\,H-O-H$$

By completely neutralizing the hypophosphoric acid with sodium hydroxide, neutral *sodium hypophosphate*, $Na_4P_2O_6$, may be formed. By adding a soluble lead salt to a solution of a hypophosphate, insoluble *lead hypophosphate*, $Pb_2P_2O_6$, may be precipitated, from which *hypophosphoric acid*, $H_4P_2O_6$, may be formed by the action of hydrogen sulphide. The acid thus obtained may be concentrated as a colorless, sirupy liquid.

Hypophosphoric acid, $H_4P_2O_6$, when warmed with water, or when acted upon by common acids, forms orthophosphoric acid, H_3PO_4, and phosphorous acid, H_3PO_3, by hydrolysis.

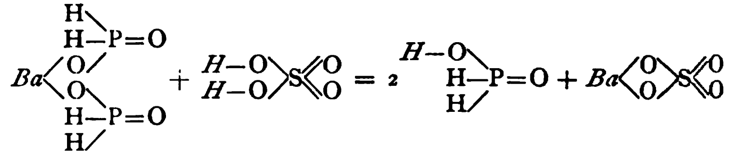


Hypophosphorous Acid and Hypophosphites.

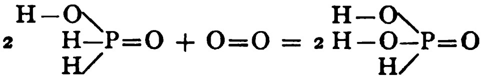
Hypophosphorous acid, H_3PO_2, is a colorless, sirupy liquid, forming at low temperature large white crystals, which melt at 17.4°. When we act upon phosphorus with a basic hydroxide in the presence of water, a hypophosphite of the characteristic element of the base is formed, while phosphorus trihydride, PH_3, is evolved. Thus, when we act upon phosphorus with a boiling solution of barium hydroxide, $Ba(OH)_2$, we get a solution of *barium hypophosphite*, $Ba(H_2PO_2)_2$, and gaseous phosphorus trihydride, PH_3.

$$3\,Ba(OH)_2 + 8\,P + 6\,H_2O = 3\,Ba(H_2PO_2)_2 + 2\,PH_3$$

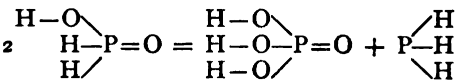
By the action of sulphuric acid upon barium hypophosphite, *hypophosphorous acid*, H_3PO_2, is obtained which, from the composition of its salts, appears, like phosphorous acid, to be a monobasic acid.



Hypophosphorous acid, H_3PO_2, when exposed to air, oxidizes to phosphorous acid,

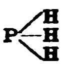


while chlorine and other strong oxidizing agents change it into orthophosphoric acid. When heated hypophosphorous acid forms orthophosphoric acid and phosphorus trihydride, PH_3.



Binary Phosphorus Compounds.

Phosphorus forms binary compounds with hydrogen, chlorine, and with some metals. The phosphorus hydrides may be made by the action of reagents upon phosphorus, and also *by the decomposition of suitable phosphorus compounds under proper conditions.*



Phosphorus trihydride, or *phosphine*, PH_3, may be made by the action of nascent hydrogen upon phosphorus.

$$2\,P + 3\,H_2 = 2\,PH_3$$

In order to secure this combination of the hydrogen with phosphorus, it is necessary to evolve the hydrogen in the presence of phosphorus, as, for example, by gently warming dilute sulphuric acid with zinc and phosphorus.

$$2\,P + 3\,H_2SO_4 + 3\,Zn = 2\,PH_3 + 3\,ZnSO_4$$

The phosphorus trihydride may be made to better advantage, however, by heating phosphorus with a concentrated solution of an alkali hydroxide, such as sodium hydroxide, when sodium hypophosphite, NaH_2PO_2, is formed in the solution, and the gaseous phosphorus trihydride, PH_3, mixed with some hydrogen and small amounts of another hydride of phosphorus having the composition P_2H_4, is evolved.

$$3\,NaOH + 4\,P + 3\,H_2O = 3\,NaH_2PO_2 + PH_3$$

We have already seen that a similar action takes place when barium hydroxide, phosphorus, and water interact.

The substance P_2H_4 is spontaneously inflammable, and causes the mixture to burst into flame upon coming into contact with the air. When, however, the mixture is conducted through a cooled tube, or through alcohol or ether, the inflammable compound is condensed to a liquid, and the phosphorus trihydride thus purified does not inflame when brought into the air.

Phosphorus trihydride may be safely prepared by nearly filling a small flask with a concentrated solution of sodium hydroxide, adding a few bits of yellow phosphorus, and a little ether. The neck of the flask is then tightly fitted with a cork, containing a delivery tube, dipping under water, which is kept warm to melt any bits of phosphorus which may be carried over into the tube mechanically. Gentle heating volatilizes the ether and displaces the air, and then evolves the impure phosphine, which spontaneously inflames as it reaches the air, forming a succession of white cloud rings of finely divided phosphorus pentoxide.

Phosphorus trihydride may also be made by the decomposition of suitable phosphorus compounds. When a piece of calcium phosphide,

Ca_3P_2, or Ca_4P_2, is thrown into water, the gaseous phosphine, PH_3, together with smaller quantities of the other phosphorus hydrides, are formed by hydrolysis, and the same compounds may be formed by the action of hydrochloric acid upon the calcium phosphides.

$$Ca_3P_2 + 6\,H_2O = 2\,PH_3 + 3\,Ca(OH)_2$$
$$Ca_3P_2 + 6\,HCl = 2\,PH_3 + 3\,CaCl_2$$

When phosphorous acid, H_3PO_3, or hypophosphorous acid, H_3PO_2, are heated, phosphorus trihydride is formed, as we have already seen.

$$4\,H_3PO_3 = PH_3 + 3\,H_3PO_4$$
$$2\,H_3PO_2 = PH_3 + H_3PO_4$$

Phosphorus trihydride is a colorless gas, of specific gravity 34.03, of characteristic garlic-like odor, insoluble in water, slightly soluble in alcohol. It may be liquefied at − 85°, and solidified at − 133.5°, under ordinary pressure. It is extremely poisonous. It does not combine with oxygen under ordinary pressure, but if the pressure of a mixture of the gas and oxygen be suddenly lowered, an explosion occurs.

The liquid hydride of phosphorus, P_2H_4, formed in small quantities with phosphorus trihydride, when the latter is made by acting upon sodium hydroxide with phosphorus, is colorless, of specific gravity 1.012, boiling at 57°, insoluble in water. It inflames spontaneously in air, burning with brilliancy. A yellow solid, P_4H_2, is also known.

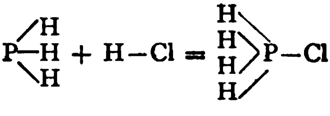
When heated to 100° with oxygen or air, phosphorus trihydride, PH_3, burns with a bright flame, forming water and white clouds of phosphorus pentoxide, P_2O_5.

$$2\,PH_3 + 4\,O_2 = P_2O_5 + 3\,H_2O$$

It explodes violently when brought into contact with chlorine, forming phosphorus trichloride, PCl_3, and hydrogen chloride.

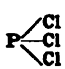
$$PH_3 + 3\,Cl_2 = PCl_3 + 3\,HCl$$

Phosphorus trihydride combines with hydrochloric acid, at very low temperature or at high pressure, to form *phosphonium chloride*, PH_4Cl, a compound in which the group PH_4 is a positive ion.



$$P\begin{smallmatrix}-H\\-H\\-H\end{smallmatrix} + H-Cl = \begin{smallmatrix}H\\H\\H\\H\end{smallmatrix}\!>P-Cl$$

Phosphonium iodide, PH_4I, is also known, and is more easily prepared than the corresponding chloride.

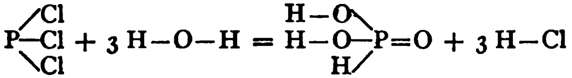


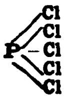
Phosphorus trichloride and phosphorus pentachloride may be made by the direct combination of phosphorus with chlorine.

When a stream of dry chlorine is passed through a quantity of phosphorus, heated in a retort, *phosphorus trichloride*, PCl_3, distills over, and may be condensed to a mobile colorless liquid, of specific gravity 1.613 at 0°, solidifying at – 112°, boiling at 76°.

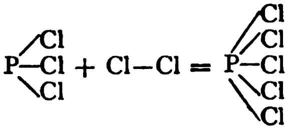
$$2\,P + 3\,Cl_2 = 2\,PCl_3$$

Phosphorus trichloride has a characteristic pungent odor, and fumes strongly in air. It is readily hydrolyzed, with the formation of phosphorous acid, H_3PO_3, and hydrochloric acid, HCl.



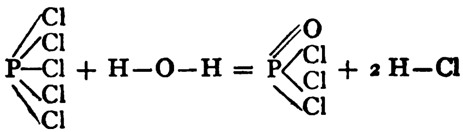


When a stream of dry chlorine is brought in contact with phosphorus trichloride, PCl_3, kept cool by water, *phosphorus pentachloride*, PCl_5, is formed as a yellowish white crystalline solid, fuming strongly in the air.

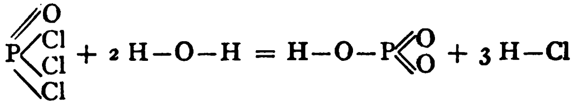


It sublimes, without melting, when gently heated, partially dissociating into phosphorus trichloride and chlorine.

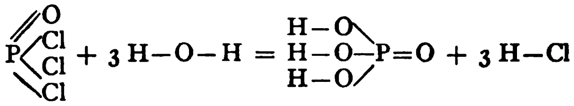
When exposed to moist air, phosphorus pentachloride, PCl_5, is hydrolyzed, forming *phosphorus oxychloride*, $POCl_3$, a colorless liquid at ordinary temperatures,



which will act energetically upon more water, forming metaphosphoric acid, HPO_3,

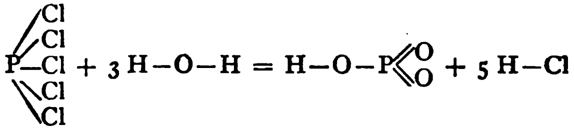


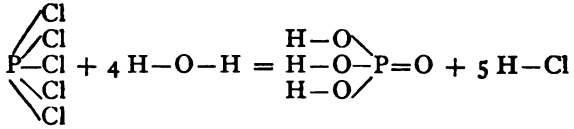
or orthophosphoric acid, H_3PO_4,



according to the proportions of the reacting substances and conditions of temperature.

Phosphorus pentachloride, PCl_5, will act upon the excess of water, forming either metaphosphoric acid, HPO_3, or orthophosphoric acid, H_3PO_4, according to the conditions.





When we act upon orthophosphorous acid, H_3PO_3, with phosphorus pentachloride, PCl_5, we get phosphorus trichloride, PCl_3, phosphorus oxychloride, $POCl_3$, and hydrochloric acid, HCl.

$$H_3PO_3 + 3\ PCl_5 = PCl_3 + 3\ POCl_3 + 3\ HCl$$

Phosphorus pentachloride acts similarly upon other oxides and hydroxides, replacing oxygen or hydroxyl by chlorine. Thus, with sulphur trioxide, SO_3, it forms *sulphuryl chloride*, SO_2Cl_2,

$$SO_3 + PCl_5 = SO_2Cl_2 + POCl_3$$

and with sulphuric acid it forms *chlorsulphonic acid*, $HClSO_3$.

$$H_2SO_4 + PCl_5 = HClSO_3 + POCl_3 + HCl$$

On account of this peculiar action in substituting chlorine for oxygen or for hydroxyl, phosphorus pentachloride finds use in the synthesis of many carbon compounds.

Phosphorus trifluoride, PF_3, *phosphorus pentafluoride*, PF_5, colorless gases; *phosphorus tribromide*, PBr_3, a colorless liquid; *phosphorus pentabromide*, PBr_5, a yellow solid; and *phosphorus triiodide*, PI_3, a red solid, are among the other binary compounds of phosphorus which are in many respects similar to the phosphorus chlorides. A number of solid sulphides of phosphorus, the most important of which are *phosphorus trisulphide*, P_2S_3, and *phosphorus pentasulphide*, P_2S_5, may be formed by heating together phosphorus and sulphur. Certain compounds of phosphorus with metals, known as *phosphides*, such as the two *calcium phosphides*, Ca_3P_2 and Ca_2P_2, may be prepared by the action of phosphorus upon metals or their compounds.

Summary. *We note in regard to the phosphorus compounds that phosphorus pentoxide and phosphorus trioxide are white solids, soluble in water with formation of colorless phosphoric acid or phosphorous acid. Orthophosphoric acid may be decomposed by heat, forming pyrophosphoric acid or metaphosphoric acid; orthophosphoric acid and pyrophosphoric acid will form neutral and acidic salts, and metaphosphoric acid will form neutral salts; the orthophosphates may be decomposed by heating, forming pyrophosphates or metaphosphates. The phosphates of the alkali elements are white solids, soluble in water; some phosphates are insoluble, and some are colored.*

Hypophosphoric acid may be made by oxidizing phosphorus, while hypophosphorous acid is made from the salt obtained by acting upon a basic hydroxide with phosphorus; both of these acids form salts.

The binary compounds of phosphorus, the gaseous phosphorus trihydride, the liquid phosphorus trichloride, and the solid phosphorus pentachloride may be made by acting upon phosphorus with suitable reagents. Phosphorus trihydride is inflammable; the phosphorus chlorides are active chemically, forming with water phosphorus oxychloride and one or more of the phosphorus acids. Chlorides, bromides, iodides, and sulphide of phosphorus as well as the phosphides of various metals are also known.

Manufacture of Phosphorus. After our study of phosphorus compounds, the processes for the *manufacture of phosphorus* may be more readily understood. There are two methods for preparing phosphorus from the native tricalcium orthophosphate found in phosphatic rocks, and bones.

First Method. According to the first method, the insoluble calcium orthophosphate, $Ca_3(PO_4)_2$, *rock phosphate*, or *bone ash*, is warmed with two thirds of its weight of concentrated sulphuric acid, by which it is changed into the readily soluble calcium hydrogen orthophosphate, $CaH_4(PO_4)_2$, which is removed from the moderately soluble calcium sulphate, formed at the same time, by washing with hot water.

$$Ca_3(PO_4)_2 + 2\ H_2SO_4 = CaH_4(PO_4)_2 + 2\ CaSO_4$$

The solution of calcium hydrogen orthophosphate is evaporated in lead pans, mixed thoroughly with powdered charcoal, dried over a direct fire, and finally heated to redness in earthenware retorts placed in a furnace. The first heating changes the acidic phosphate into calcium metaphosphate, $Ca(PO_3)_2$, which is subsequently reduced by the action of the charcoal, a residue of calcium orthophosphate being formed, while the phosphorus vapor is distilled and condensed in closed vessels, the carbon monoxide being allowed to escape.

$$CaH_4(PO_4)_2 = Ca(PO_3)_2 + 2\ H_2O$$

$$3\ Ca(PO_3)_2 + 10\ C = 4\ P + Ca_3(PO_4)_2 + 10\ CO$$

A larger yield of phosphorus may be obtained by adding a quantity of sand to the mixture and then heating in an electric furnace, when a complete decomposition of the calcium metaphosphate, $Ca(PO_3)_2$, results, a residue of calcium metasilicate, $CaSiO_3$, being formed, while phosphorus and carbon monoxide are set free.

$$Ca(PO_3)_2 + 5\ C + SiO_2 = 2\ P + CaSiO_3 + 5\ CO$$

Second Method. According to a second method, the insoluble calcium orthophosphate may be treated with an excess of dilute sulphuric acid, orthophosphoric acid, H_3PO_4, and calcium sulphate, $CaSO_4$, being slowly formed.

$$Ca_3(PO_4)_2 + 3\ H_2SO_4 = 2\ H_3PO_4 + 3\ CaSO_4$$

The calcium sulphate which is precipitated in the reaction is removed by filtration, and the remaining phosphoric acid solution is concentrated by heating in lead tanks, when more of the calcium sulphate is deposited as a residue, from which the acid may be decanted. The concentrated solution of phosphoric acid is mixed with carbon (charcoal, coke, sawdust) in iron pots, dried over a fire, and finally heated to incandescence for many hours in earthenware retorts in a furnace. The phosphorus vapor, containing impurities, passes through earthenware pipes into water, where the phosphorus is condensed.

The heating first changes the orthophosphoric acid, H_3PO_4, into metaphosphoric acid, HPO_3, which becomes subsequently reduced by the carbon with the formation of phosphorus and a mixture of hydrogen and carbon monoxide, CO.

$$H_3PO_4 = HPO_3 + H_2O$$
$$2\,HPO_3 + 6\,C = 2\,P + 6\,CO + H_2$$

Arsenic, As, 75.0

Arsenic Ores. Arsenic is found both free and in combination, and usually in association with the minerals of other elements in veins of crystalline rocks. Besides the native *arsenic*, the most important arsenic minerals are the double sulphide of arsenic and iron, *mispickel*, FeAsS, and the oxide, *arsenolite*, As_2O_3. Other arsenic minerals are *realgar*, As_2S_2, and *orpiment*, As_2S_3.

Free arsenic may be obtained from *mispickel*, FeAsS, by roasting the ore with iron in earthenware retorts connected with receivers in which the vaporized arsenic condenses as a solid sublimate, while a residue of ferrous sulphide, FeS, remains in the retort.

$$2\,FeAsS = 2\,As + 2\,FeS$$

From the *arsenolite*, As_2O_3, the arsenic may be obtained by heating with powdered charcoal, when carbon monoxide, CO, is formed and a residue of arsenic is left behind.

$$As_2O_3 + 3\,C = 2\,As + 3\,CO$$

Allotropic Forms of Arsenic. *Arsenic* exists in two allotropic modifications—a black, nearly lusterless, *amorphous solid* of specific gravity 4.71, and as gray-white *hexagonal crystals* of specific gravity 5.73, which are brittle and readily powdered. When the crystalline arsenic is heated in a glass tube in a current of hydrogen, it forms a sublimate of the amorphous arsenic, which may be changed into the crystalline form by heating out of contact with oxygen to 360°. Arsenic can be melted by heating it to 500° under pressure in a sealed tube. When heated under ordinary pressure, it forms at 450° a yellow vapor having a characteristic garlic-like odor. Arsenic remains unaltered in dry air, but becomes tarnished in moist air, and when heated to 180° in air or oxygen, burns with a bluish light, forming arsenic trioxide. It will combine directly with most of the elements, forming binary compounds. It is slowly acted upon by nitric acid. It is alloyed with lead in shot, and is used in making fireworks.

The determination of the specific gravity of arsenic vapor has thrown light upon the behavior of arsenic at high temperature. Thus, at 860° arsenic vapor has a specific gravity of nearly 300, corresponding to the molecular symbol As_4, while at 1736° the specific gravity is a little above 150, which corresponds to the symbol As_2. Evidently the molecules of arsenic, which at ordinary temperature consist of four atoms, are at high temperature dissociated into molecules containing two atoms each.

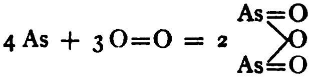
Oxides and Hydroxides. *From arsenic may be prepared the two oxides and the several hydroxides of arsenic.* Thus we have:

OXIDES	HYDROXIDES
Arsenic trioxide, As_2O_3 or As_4O_6	Arsenious acid, H_3AsO_3*
	[Metarsenious acid, $HAsO_2$] †
Arsenic pentoxide, As_2O_5	Orthoarsenic acid, H_3AsO_4
	Pyroarsenic acid, $H_4As_2O_7$
	Metarsenic acid, $HAsO_3$

* Known in solution only. † Unknown, but represented by salts.

The lower oxide, arsenic trioxide, As_2O_3 or As_4O_6 according to temperature, is formed when arsenic is heated in oxygen or air, and its solution in water we may call arsenious acid, H_3AsO_3, although such a compound cannot be prepared in free condition. Arsenic pentoxide, As_2O_5, may be formed by gentle ignition of the hydroxide formed by the action of oxidizing agents upon either arsenic or the lower oxide, and from it may be formed orthoarsenic acid, H_3AsO_4, which, when heated, will give the two oxyacids, pyroarsenic acid, $H_4As_2O_7$, and metarsenic acid, $HAsO_3$. The two arsenic oxides are anhydrides, since they will combine with water to form the corresponding acidic hydroxides.

Arsenic Trioxide. *Arsenic trioxide*, or *arsenious oxide*, As_2O_3, or As_4O_6 (white arsenic), occurs in nature as the mineral ***arsenolite***. It is formed when arsenic burns in oxygen or air.

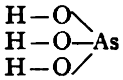


$$4\,As + 3\,O{=}O = 2\begin{matrix} As{=}O \\ \;\;>O \\ As{=}O \end{matrix}$$

Arsenic trioxide exists as an amorphous transparent glassy mass of specific gravity 3.74, and as opaque crystals of two varieties. The amorphous oxide gradually changes into a crystalline variety, while the crystalline forms may be changed into the glassy form by heating. Arsenic trioxide may be melted by heating under high pressure; when heated to 218° under ordinary pressure it forms a vapor, which, when cooled, condenses into a crystalline sublimate. Arsenic trioxide is slightly soluble in water, is readily acted upon by bases and acids and by solutions of alkali carbonates.

Arsenic trioxide is exceedingly poisonous. It acts as an irritant poison, although those who are accustomed to taking it are able to withstand successive doses in increasingly large amounts. Freshly precipitated ferric hydroxide, which makes an insoluble compound with arsenic trioxide, is employed as an antidote against arsenic poisoning. Arsenic trioxide is made in large quantities by roasting arsenic ores, and is used in making pigments and glass, and various substances used as poisons.

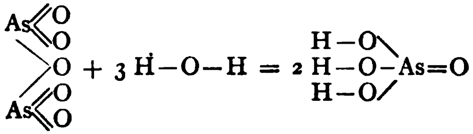
The solution of arsenic trioxide, As_2O_3, in water, acts like a tribasic acid, so we call it *arsenious acid*, H_3AsO_3, expressed graphically by the symbol



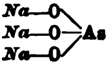
The specific gravity of arsenic trioxide vapor at temperatures between 500° and 700° is nearly 396, corresponding to the molecular symbol As_4O_6, while above 1800° the observed specific gravity of nearly 198 points to the complete dissociation of the vapor into molecules having the symbol As_2O_3. We may represent the constitution of both the dissociated and the undissociated arsenic trioxide graphically, by symbols similar to those employed to represent phosphorus trioxide.

Arsenic Pentoxide. *Arsenic pentoxide*, As_2O_5, formed by heating arsenic acid, is a white solid, of specific gravity 3.7, very slowly soluble in water, and deliquescent in moist air.

Arsenic pentoxide combines with water to form soluble *orthoarsenic acid*, H_3AsO_4.



Arsenious Acid and Arsenites.



Arsenious acid reacts with bases, forming the arsenites, in which arsenic is a constituent of the negative ion. When arsenious acid, H_3AsO_3, is acted upon by sodium hydroxide in suitable proportions, the neutral *sodium arsenite*, Na_3AsO_3, is formed.

$$3\,\mathit{Na}\mathrm{OH} + \mathit{H}_3\mathrm{AsO}_3 = \mathit{Na}_3\mathrm{AsO}_3 + 3\,\mathrm{H_2O}$$

With other proportions of the reacting substances, the acidic salts, *disodium hydrogen arsenite*, Na_2HAsO_3,

$$2\,\mathit{Na}\mathrm{OH} + \mathit{H}_2\mathrm{HAsO}_3 = \mathit{Na}_2\mathrm{HAsO}_3 + 2\,\mathrm{H_2O}$$

and *sodium dihydrogen arsenite*, NaH_2AsO_3, may be obtained.

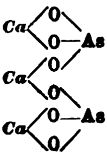
$$\mathit{Na}\mathrm{OH} + \mathit{H}\mathrm{H_2AsO_3} = \mathit{Na}\mathrm{H_2AsO_3} + \mathrm{H_2O}$$

When the sodium dihydrogen arsenite, NaH_2AsO_3, is heated, one equivalent of water is removed, and a residue of *sodium metarsenite*, $NaAsO_2$, corresponding to an unknown metarsenious acid, remains behind.

$$\mathrm{NaH_2AsO_3} = \mathrm{NaAsO_2} + \mathrm{H_2O}$$

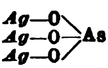
Potassium hydroxide reacts similarly with arsenious acid to form neutral and acidic arsenites, and by ignition of the potassium dihydrogen arsenite a potassium metarsenite may be obtained. The alkali arsenites are generally white, soluble in water, and extremely poisonous. A solution of the two acidic potassium arsenites is a mixture known in medicine as *Fowler's solution.*

Insoluble Arsenites.



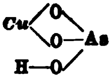
Certain arsenites are insoluble and may be produced as characteristic precipitates. A soluble calcium salt, such as calcium chloride, $CaCl_2$, produces in a solution of a soluble arsenite, such as sodium arsenite, Na_3AsO_3, a white precipitate of *calcium arsenite*, $Ca_3(AsO_3)_2$, which may be acted upon by acids.

$$2\,\mathrm{Na_3AsO_3} + 3\,\mathrm{CaCl_2} = \mathbf{Ca_3(AsO_3)_2} + 6\,\mathrm{NaCl}$$



Silver nitrate, $AgNO_3$, and other soluble silver salts, will precipitate yellow *silver arsenite*, Ag_3AsO_3, from a solution of sodium arsenite, Na_3AsO_3, or other soluble arsenites

$$\mathrm{Na_3AsO_3} + 3\,\mathrm{AgNO_3} = \mathbf{Ag_3AsO_3} + 3\,\mathrm{NaNO_3}$$



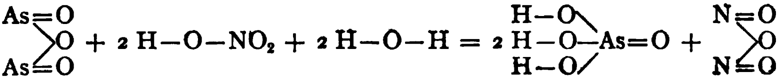
When we add a solution of cupric sulphate, $CuSO_4$, or other soluble cupric salt, to a solution of sodium arsenite or other soluble arsenite, we get a grass-green precipitate of *copper hydrogen arsenite*, $CuHAsO_3$, which may be acted upon by alkali hydroxides and by acids.

$$Na_2HAsO_3 + CuSO_4 = CuHAsO_3 + Na_2SO_4$$

This is *Scheele's green*, used as a pigment. *Paris green* or *Emerald green*, used largely as a poison, is a compound of cupric arsenite and cupric acetate.

When arsenious acid, or a solution of sodium arsenite, or other soluble arsenite, is added to freshly precipitated ferric hydroxide, $Fe(OH)_3$, held in suspension in water, a dark red precipitate of an insoluble basic *ferric arsenite*, resembling the ferric hydroxide in appearance, is formed. Upon the insolubility and inertness of this substance depends the use of freshly precipitated ferric hydroxide as an antidote against arsenic poisoning.

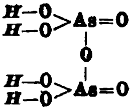
Arsenic Acid. *By the action upon arsenic trioxide of oxidizing agents arsenic acid is formed.* When arsenic trioxide, As_2O_3, is acted upon by nitric acid, diluted with one third its volume of water and warmed, nitrogen trioxide, N_2O_3, passes off, and *orthoarsenic acid*, H_3AsO_4, remains in solution.



$$\begin{array}{l}As=O\\ \quad >O\\ As=O\end{array} + 2\,H-O-NO_2 + 2\,H-O-H = 2\,\begin{array}{l}H-O\\ H-O-As=O\\ H-O\end{array} + \begin{array}{l}N=O\\ \quad >O\\ N=O\end{array}$$

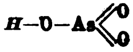
By evaporating the solution thus obtained, crystals may be recovered which have the composition $(H_3AsO_4)_2 \cdot H_2O$, are soluble in water, melt at 100°, and effloresce at ordinary temperature, becoming the anhydrous H_3AsO_4.

Oxyarsenic Acids. When orthoarsenic acid, H_3AsO_4, is heated to 140–180° it forms *pyroarsenic acid*, $H_4As_2O_7$, water being evolved.



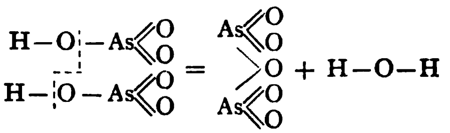
$$2\,H_3AsO_4 = H_4As_2O_7 + H_2O$$

When pyroarsenic acid is heated to 200° water is evolved, and *metarsenic acid*, $HAsO_3$, remains.

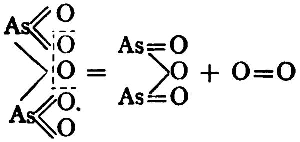


$$H_4As_2O_7 = 2\,HAsO_3 + H_2O$$

When metarsenic acid is heated to redness, water is evolved, and a glassy mass of *arsenic pentoxide*, As_2O_5, remains,

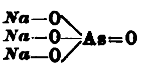


and arsenic pentoxide, when strongly heated, evolves oxygen, leaving a residue of *arsenic trioxide*, As_2O_3.



As has been shown, arsenic pentoxide decomposes when heated, forming arsenic trioxide and oxygen. It may be reduced to arsenic by heating with charcoal or some other reducing agent.

Interaction of Arsenic Acids with Bases. *Orthoarsenic acid neutralizes bases to form orthoarsenates, salts richer in oxygen than the arsenites, and in which arsenic is in the negative ion.* When we add sodium hydroxide to a solution of orthoarsenic acid, H_3AsO_4, we may obtain from the solution either *sodium orthoarsenate*, Na_3AsO_4,



$$3\,NaOH + H_3AsO_4 = Na_3AsO_4 + 3\,H_2O$$

or *disodium hydrogen orthoarsenate*, Na_2HAsO_4,

$$2\,NaOH + H_2HAsO_4 = Na_2HAsO_4 + 2\,H_2O$$

or *sodium dihydrogen orthoarsenate*, NaH_2AsO_4,

$$NaOH + HH_2AsO_4 = NaH_2AsO_4 + H_2O$$

according to the proportions in which the substances react.

Potassium orthoarsenates may be prepared similarly. The alkali arsenates are white soluble salts. Sodium orthoarsenate is used in calico printing.

Oxidation of Arsenites. *Orthoarsenates may also be formed by the action of oxidizing agents upon arsenites.* Thus, when chlorine acts upon sodium arsenite, Na_3AsO_3, in presence of sodium hydroxide, or sodium carbonate, *sodium orthoarsenate*, Na_3AsO_4, is formed.

$$Na_3AsO_3 + 2\,NaOH + Cl_2 = Na_3AsO_4 + 2\,NaCl + H_2O$$

$$Na_3AsO_3 + Na_2CO_3 + Cl_2 = Na_3AsO_4 + 2\,NaCl + CO_2$$

A similar action will take place between an acidic arsenite, such as sodium dihydrogen arsenite, NaH_2AsO_3, and chlorine, in the presence of the sodium hydrogen carbonate, the acidic *sodium dihydrogen orthoarsenate*, NaH_2AsO_4, being formed in this case.

$$NaH_2AsO_3 + 2\,NaHCO_3 + Cl_2 = NaH_2AsO_4 + 2\,NaCl + H_2O + 2\,CO_2$$

With the corresponding salts of potassium and other elements similar reactions may be brought about. Iodine and similar elements, and sodium hypochlorite, NaOCl, and like compounds, will exert a similar oxidizing action upon arsenites in alkaline solution.

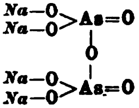
Oxysalts.

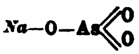
The acidic orthoarsenates may be decomposed by heating, with the formation of pyroarsenates and metarsenates, oxysalts corresponding to pyroarsenic acid and metarsenic acid respectively. When disodium hydrogen orthoarsenate, Na_2HAsO_4, is carefully heated, it loses water, forming *sodium pyroarsenate*, $Na_4As_2O_7$,

$$2\,Na_2HAsO_4 = Na_4As_2O_7 + H_2O$$

and by heating sodium dihydrogen orthoarsenate, NaH_2AsO_4, *sodium metarsenate*, $NaAsO_3$, is formed in similar manner.

$$NaH_2AsO_4 = NaAsO_3 + H_2O$$



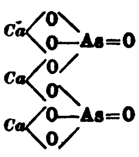


Both the sodium pyroarsenate and the sodium metarsenate, however, when dissolved in water, form at once sodium orthoarsenate.

Insoluble Arsenates.

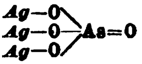
Arsenates of some elements are insoluble, and may be formed as characteristic precipitates. When to a solution of an arsenate, such as sodium orthoarsenate, Na_3AsO_4, an excess of a soluble calcium salt, such as calcium chloride, is added, a precipitate of white *calcium orthoarsenate*, $Ca_3(AsO_4)_2$, is formed.

$$2\,Na_3AsO_4 + 3\,CaCl_2 = \mathbf{Ca_3(AsO_4)_2} + 6\,NaCl$$



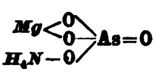
When calcium chloride is added to a solution of an acidic arsenate, such as disodium hydrogen orthoarsenate, Na_2HAsO_4, a white precipitate of *calcium hydrogen orthoarsenate*, $CaHAsO_4$, may be obtained.

$$Na_2HAsO_4 + CaCl_2 = \mathbf{CaHAsO_4} + 2\,NaCl$$



By the addition of silver nitrate, $AgNO_3$, or some other soluble silver salt, to a solution of orthoarsenic acid, H_3AsO_4, or of an arsenate, such as sodium arsenate, Na_3AsO_4, reddish brown *silver orthoarsenate*, Ag_3AsO_4, readily acted upon by excess of dilute nitric acid and by ammonium hydroxide, is precipitated.

$$H_3AsO_4 + 3\ AgNO_3 = \mathbf{Ag_3AsO_4} + 3\ HNO_3$$
$$Na_3AsO_4 + 3\ AgNO_3 = \mathbf{Ag_3AsO_4} + 3\ NaNO_3$$



When to a solution of orthoarsenic acid, H_3AsO_4, containing ammonium chloride, NH_4Cl, or some other ammonium salt, and ammonium hydroxide in sufficient amount, we add a soluble salt of magnesium, such as magnesium sulphate, $MgSO_4$, a finely crystalline white precipitate of *magnesium ammonium orthoarsenate*, $Mg(NH_4)AsO_4$, is formed.

$$H_3AsO_4 + MgSO_4 + 3\ NH_4OH = \mathbf{Mg(NH_4)AsO_4} + (NH_4)_2SO_4 + 3\ H_2O$$

The presence of the ammonium salt prevents the precipitation of magnesium hydroxide. Various other insoluble arsenates, beside those that have been described, may be prepared.

Reduction of Orthoarsenic Acid and Orthoarsenates.

Orthoarsenic acid and the orthoarsenates may be acted upon by some reducing agents, being thereby changed into arsenious acid and arsenites respectively. When orthoarsenic acid, H_3AsO_4, is acted upon by sulphurous acid, H_2SO_3, arsenious acid, H_3AsO_3, and sulphuric acid are formed.

$$H_3AsO_4 + H_2SO_3 = H_3AsO_3 + H_2SO_4$$

When orthoarsenic acid is acted upon by hydriodic acid, HI, arsenious acid, H_3AsO_3, is formed and iodine is set free.

$$H_3AsO_4 + 2\ HI = H_3AsO_3 + H_2O + I_2$$

Similarly, hydrobromic acid, HBr, reduces orthoarsenic acid, H_3AsO_4, to arsenious acid, H_3AsO_3, with the liberation of bromine.

$$H_3AsO_4 + 2\ HBr = H_3AsO_3 + H_2O + Br_2$$

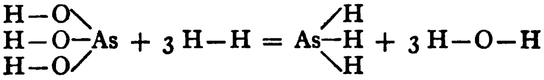
These reactions are useful in analysis.

Binary Arsenic Compounds.

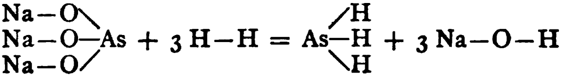
Certain binary compounds of arsenic may be formed by the action of reagents upon arsenic compounds.

Arsenic Trihydride.

Arsenic trihydride, AsH_3 (arsine), may be formed by the action of nascent hydrogen upon arsenious acid, H_3AsO_3, or upon a soluble arsenite such as sodium arsenite, Na_3AsO_3.



$$\begin{matrix} H-O\diagdown \\ H-O-As \\ H-O\diagup \end{matrix} + 3\,H-H = As\begin{matrix} \diagup H \\ -H \\ \diagdown H \end{matrix} + 3\,H-O-H$$

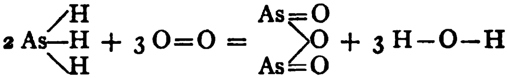


$$\begin{matrix} Na-O\diagdown \\ Na-O-As \\ Na-O\diagup \end{matrix} + 3\,H-H = As\begin{matrix} \diagup H \\ -H \\ \diagdown H \end{matrix} + 3\,Na-O-H$$

In practice, arsenic trihydride may be prepared in pure condition by acting upon an alloy of zinc and arsenic with hydrochloric acid; and in mixture with hydrogen it may be prepared by pouring a solution of an arsenite into a generator from which hydrogen is being evolved by action of a dilute acid or a strong basic hydroxide upon zinc or aluminium.

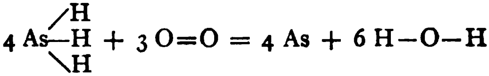
Arsenic trihydride is a colorless gas, of strong characteristic odor, resembling that of garlic. Cold and pressure convert it to a colorless liquid, boiling at −55°, and even to a colorless solid which melts at −113.5°. It is extremely poisonous.

Arsenic trihydride is inflammable, burning with a bluish white flame when ignited, white clouds of arsenic trioxide being evolved.



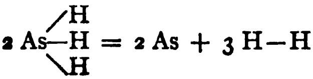
$$2\,As\begin{matrix} \diagup H \\ -H \\ \diagdown H \end{matrix} + 3\,O=O = \begin{matrix} As=O \\ \rangle O \\ As=O \end{matrix} + 3\,H-O-H$$

If a cold body, such as a piece of porcelain, be held in a flame of burning arsenic trihydride, cutting off the supply of oxygen from the side of the flame next the porcelain, the temperature will be so far reduced that the oxidation will be but partial, and black spots or "mirrors" of arsenic will be formed on the porcelain.



$$4\,As\begin{matrix} \diagup H \\ -H \\ \diagdown H \end{matrix} + 3\,O=O = 4\,As + 6\,H-O-H$$

When a stream of arsenic trihydride is passed through a small glass tube, contracted to small diameter, and heated to 230°, it is decomposed, arsenic being deposited as the characteristic mirror on the walls of the tube, and hydrogen being evolved.



$$2\,As\begin{matrix} \diagup H \\ -H \\ \diagdown H \end{matrix} = 2\,As + 3\,H-H$$

The mirror of arsenic deposited by the oxidation or decomposition of arsenic trihydride is readily removed by a solution of sodium hypochlorite, NaOCl, with formation of arsenic acid and sodium chloride.

$$2\,As + 5\,NaOCl + 3\,H_2O = 2\,H_3AsO_4 + 5\,NaCl$$

The arsenic mirror is also removed by a mixture of ammonium sulphide, $(NH_4)_2S$, and sulphur.

Marsh Test for Arsenic Compounds. The production of a visible arsenic mirror by extremely small quantities of arsenic trihydride is turned to useful account in the *Marsh test* for arsenic compounds.

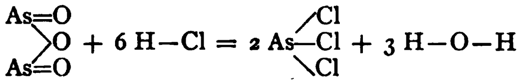
For the examination of substances in which an arsenic compound may be present in readily appreciable amounts, the test may be made by placing a few granules of zinc in a test-tube, covering with dilute hydrochloric acid or sulphuric acid in amount sufficient to set up a brisk evolution of hydrogen, introducing a little of the substance to be examined, best in solution, quickly placing a loose plug of cotton above the liquid, stopping the tube with a cork bearing a short glass delivery tube drawn out to a fine jet, and immediately igniting the stream of gases issuing from the tube, taking care throughout the experiment to avoid breathing the gas from the tube. The cotton plug serves the double purpose of partially drying the evolved gases, and of preventing an explosion in case air enough still remains in the tube to make an explosive mixture when the flame is applied. In case arsenic compounds were present in the original substance, the characteristic mirror will be deposited upon a cold piece of porcelain held within the flame of burning gas.

To make the test still more delicate, a mixture of zinc and hydrochloric acid and the solution to be examined may be placed in a small generating flask, the delivery tube of which passes into a small calcium chloride drying tube which is connected at its further end with a small reduction tube of hard glass, drawn gradually to a fine jet. If the original solution contained an arsenic compound, the characteristic mirror will be deposited in the cool contracted portions of the delivery tube when the uncontracted portion of the tube is suitably heated.

Reduction by Arsenic Trihydride. *Arsenic trihydride acts as a reducer, and will precipitate some metals from solutions of their salts.* If a stream of arsenic trihydride, AsH_3, be passed into a solution of a silver salt, such as silver nitrate, $AgNO_3$, arsenious acid, H_3AsO_3, and nitric acid will be formed, and silver will be deposited.

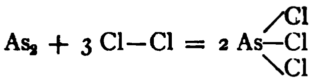
$$AsH_3 + 6\,AgNO_3 + 3\,H_2O = H_3AsO_3 + 6\,Ag + 6\,HNO_3$$

Arsenic Chlorides. *Arsenic trichloride*, $AsCl_3$, is a colorless liquid of specific gravity 2.2, boiling at 130°, forming at low temperatures a colorless solid which melts at $-18°$. It may be prepared by acting upon arsenic trioxide, As_2O_3, with concentrated hydrochloric acid.



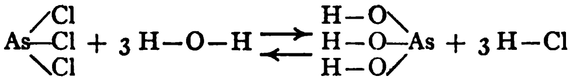
$$\begin{matrix}\mathrm{As{=}O}\\ \quad\rangle\mathrm{O}\\ \mathrm{As{=}O}\end{matrix} + 6\,\mathrm{H{-}Cl} = 2\,\mathrm{As}\begin{matrix}\diagup\mathrm{Cl}\\ -\mathrm{Cl}\\ \diagdown\mathrm{Cl}\end{matrix} + 3\,\mathrm{H{-}O{-}H}$$

When powdered arsenic is thrown into chlorine gas, it inflames with violence, forming arsenic trichloride.



$$\mathrm{As_2} + 3\,\mathrm{Cl{-}Cl} = 2\,\mathrm{As}\begin{matrix}\diagup\mathrm{Cl}\\ -\mathrm{Cl}\\ \diagdown\mathrm{Cl}\end{matrix}$$

Arsenic trichloride, $AsCl_3$, is hydrolyzed by an excess of water, forming arsenious acid, H_3AsO_3, and hydrogen chloride, but the action is reversible and conditioned by the proportions of water and hydrogen chloride present.

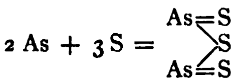


$$\mathrm{As}\begin{matrix}\diagup\mathrm{Cl}\\ -\mathrm{Cl}\\ \diagdown\mathrm{Cl}\end{matrix} + 3\,\mathrm{H{-}O{-}H} \rightleftarrows \begin{matrix}\mathrm{H{-}O}\diagdown\\ \mathrm{H{-}O}-\\ \mathrm{H{-}O}\diagup\end{matrix}\mathrm{As} + 3\,\mathrm{H{-}Cl}$$

Arsenic pentachloride, $AsCl_5$, formed by the action of chlorine upon cooled arsenic trichloride, exists in the form of yellow crystals below $-40°$, as a yellow liquid between about $-40°$ and $-25°$, decomposing into arsenic trichloride at higher temperatures.

Arsenic tribromide, $AsBr_3$, a white crystalline solid, and *arsenic triiodide*, AsI_3, red crystals, are also known.

Arsenic Sulphides. *Arsenic trisulphide*, As_2S_3 (arsenious sulphide), a brilliant yellow crystalline solid, of specific gravity 3.4, insoluble in water and unacted upon by ordinary dilute acids, is found as the mineral *orpiment*. It may be made artificially by fusing together arsenic and sulphur in such proportions that two atoms of arsenic will conbine with three atoms of sulphur.

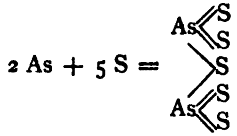


$$2\,\mathrm{As} + 3\,\mathrm{S} = \begin{matrix}\mathrm{As{=}S}\\ \quad\rangle\mathrm{S}\\ \mathrm{As{=}S}\end{matrix}$$

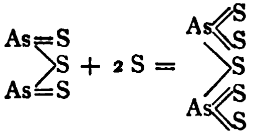
It may also be produced as a precipitate by adding hydrogen sulphide, or some other soluble sulphide, to a solution of arsenious acid in presence of a strong acid. When arsenic trisulphide is heated in a current of air, it is oxidized to arsenic trioxide, As_2O_3, while sulphur dioxide is also formed.

$$2\ As_2S_3 + 9\ O_2 = 2\ As_2O_3 + 6\ SO_2$$

Arsenic pentasulphide, As_2S_5 (arsenic sulphide), is a yellow solid, unacted upon by ordinary dilute acids. It may be made by fusing together arsenic and sulphur in proper proportions.



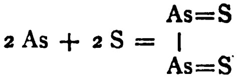
It may also be formed by fusing arsenic trisulphide, As_2S_3, with an excess of sulphur.



It may also be produced as a precipitate by adding hydrogen sulphide, or some other soluble sulphide, to a solution of arsenic acid in presence of a strong acid. When arsenic pentasulphide is heated in a current of air, it is reduced to arsenic trioxide, As_2O_3, and sulphur dioxide is formed simultaneously.

$$2\ As_2S_5 + 13\ O_2 = 2\ As_2O_3 + 10\ SO_2$$

Arsenic disulphide, As_2S_2, is a ruby-red crystalline solid of specific gravity 3.5, found as the mineral *realgar*. It may be formed by fusing arsenic with sulphur in proper proportions.



$$2\ As + 2\ S = \begin{array}{c} As{=}S \\ | \\ As{=}S \end{array}$$

It may be oxidized to arsenic trioxide by heating in air. It is used as a pigment.

Precipitation of Arsenic Sulphides. *The arsenic sulphides may be formed as characteristic precipitates by adding suitable reagents to solutions of arsenic compounds.*

Hydrogen sulphide, H_2S, or any other soluble sulphide, will precipitate yellow *arsenic trisulphide*, As_2S_3, from an acidulated solution of arsenious acid, H_3AsO_3. If, however, no other acid is present beside the arsenious acid, the arsenic trisulphide formed remains in colloidal solution, from which it is precipitated only slowly on long standing.

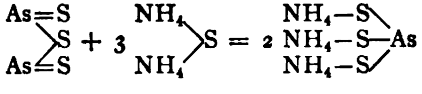
$$2\,H_3AsO_3 + 3\,H_2S = \mathbf{As_2S_3} + 6\,H_2O$$

Arsenic trisulphide may be precipitated from solutions of arsenites by hydrogen sulphide or other soluble sulphides after addition of an excess of an acid. If we add to a solution of sodium arsenite, Na_3AsO_3, an excess of hydrochloric acid, and then pass into the mixture, now containing arsenious acid and sodium chloride, hydrogen sulphide, we get a precipitate of *arsenic trisulphide*, the sodium chloride formed remaining in the solution.

$$2\,Na_3AsO_3 + 3\,H_2S + 6\,HCl = \mathbf{As_2S_3} + 6\,NaCl + 6\,H_2O$$

Ammonium sulphide, $(NH_4)_2S$, may be used to precipitate arsenic trisulphide from acidulated solutions of arsenious acid, but the precipitate thus formed will be acted upon by an excess of ammonium sulphide, with the formation of a soluble product. The precipitate of arsenic trisulphide is not acted upon by dilute hydrochloric acid, but is slowly attacked by hot concentrated hydrochloric acid.

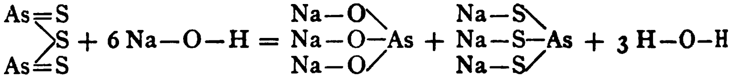
Sulpharsenites. The precipitate of arsenic trisulphide may be acted upon by ammonium sulphide, or by an alkali sulphide, with the formation of a soluble sulpharsenite, readily decomposed by the common acids, with precipitation of arsenic trisulphide and evolution of hydrogen sulphide. Thus, ammonium sulphide, $(NH_4)_2S$, acts upon arsenic trisulphide, As_2S_3, forming *ammonium sulpharsenite*, $(NH_4)_3AsS_3$, in solution,



from which by the addition of hydrochloric acid arsenic trisulphide is precipitated, while hydrogen sulphide is evolved.

$$2\,(NH_4)_3AsS_3 + 6\,HCl = As_2S_3 + 3\,H_2S + 6\,NH_4Cl$$

The precipitate of arsenic trisulphide may be acted upon by an alkali hydroxide with the formation of an equivalent mixture of a sulpharsenite and an arsenite, which remain in solution, and which may be readily decomposed by the stronger acids, with precipitation of arsenic trisulphide, but without the evolution of hydrogen sulphide. Thus, sodium hydroxide acts upon arsenic trisulphide to form ***sodium sulpharsenite***, Na_3AsS_3, and sodium arsenite, Na_3AsO_3, in solution,



$$\begin{matrix}As{=}S\\ \rangle S\\ As{=}S\end{matrix} + 6\,Na{-}O{-}H = \begin{matrix}Na{-}O\diagdown\\ Na{-}O{-}As\\ Na{-}O\diagup\end{matrix} + \begin{matrix}Na{-}S\diagdown\\ Na{-}S{-}As\\ Na{-}S\diagup\end{matrix} + 3\,H{-}O{-}H$$

from which by the action of hydrochloric acid arsenic trisulphide is precipitated.

$$Na_3AsS_3 + Na_3AsO_3 + 6\,HCl = As_2S_3 + 6\,NaCl + 3\,H_2O$$

The nature of the action of hydrogen sulphide and of other soluble sulphides upon arsenic acid or arsenates in solutions depends upon conditions of concentration of the reagents, and upon the temperature.

When hydrogen sulphide, H_2S, or any other soluble sulphide, is added to a concentrated solution of arsenic acid, H_3AsO_4, a reduction takes place, arsenious acid, H_3AsO_3, and water being formed, while sulphur is set free.

$$H_3AsO_4 + H_2S = H_3AsO_3 + H_2O + S$$

The further addition of hydrogen sulphide to the solution will precipitate *arsenic trisulphide*, As_2S_3.

When hydrogen sulphide, or other soluble sulphide, is added to a cold dilute acidulated solution of arsenic acid, H_3AsO_4, ***arsenic pentasulphide***, As_2S_5, may be slowly formed as a yellow precipitate.

$$2\,H_3AsO_4 + 5\,H_2S = \mathbf{As_2S_5} + 8\,H_2O$$

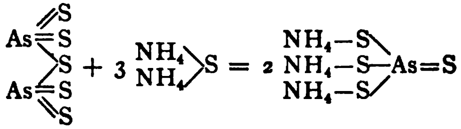
Upon heating, the precipitate tends to decompose into ***arsenic trisulphide***, As_2S_3, and sulphur.

Arsenic pentasulphide, As_2S_5, may be precipitated from solution of arsenates by hydrogen sulphide or other soluble sulphides in the presence of acids. When we add to a solution of sodium arsenate, Na_3AsO_4, an excess of hydrochloric acid, and then pass into the mixture, now containing arsenic acid and sodium chloride, hydrogen sulphide, H_2S, we get a precipitate of *arsenic pentasulphide*, As_2S_5, or of *arsenic trisulphide*, As_2S_3, and sulphur, according to conditions of concentration, sodium chloride remaining in solution.

$$2\,Na_3AsO_4 + 5\,H_2S + 6\,HCl = \mathbf{As_2S_5} + 6\,NaCl + 8\,H_2O$$

Ammonium sulphide, $(NH_4)_2S$, may be used to precipitate arsenic pentasulphide from acidulated solution of arsenic acid, but the precipitate thus formed will be acted upon by an excess of ammonium sulphide, with the formation of a soluble product. The precipitate of arsenic pentasulphide is not acted upon by dilute hydrochloric acid, but may be attacked by boiling concentrated hydrochloric acid.

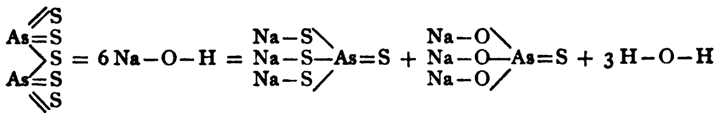
Sulpharsenates. The precipitate of arsenic pentasulphide may be acted upon by ammonium sulphide, or by an alkali sulphide, with the formation of a soluble sulpharsenate, readily decomposed by the common acids, with precipitation of arsenic pentasulphide, which, if the conditions favor, may be further decomposed into arsenic trisulphide and sulphur. Thus, ammonium sulphide, $(NH_4)_2S$, acts upon arsenic pentasulphide, As_2S_5, forming *ammonium sulpharsenate*, $(NH_4)_3AsS_4$, in solution,



from which, by the addition of hydrochloric acid, arsenic pentasulphide, As_2S_5, or arsenic trisulphide, As_2S_3, and sulphur, may be precipitated, while hydrogen sulphide is evolved.

$$2\,(NH_4)_3AsS_4 + 6\,HCl = As_2S_5 + 3\,H_2S + 6\,NH_4Cl$$

The precipitate of arsenic pentasulphide may be acted upon by an alkali hydroxide, with the formation of an equivalent mixture of a sulpharsenate and a sulphoxyarsenate which remain in solution, and which may be readily decomposed by the common acids, with precipitation of arsenic pentasulphide, or of arsenic trisulphide and sulphur, but without the evolution of hydrogen sulphide. Thus, sodium hydroxide acts upon arsenic pentasulphide to form *sodium sulpharsenate*, Na_3AsS_4, and *sodium sulphoxyarsenate*, Na_3AsSO_3, in solution,



from which, by the addition of hydrochloric acid, arsenic pentasulphide, As_2S_5, or arsenic trisulphide, As_2S_3, and sulphur, may be precipitated.

$$Na_3AsS_4 + Na_3AsSO_3 + 6\,HCl = As_2S_5 + 6\,NaCl + 3\,H_2O$$

Sodium metasulpharsenate, $NaAsS_3$, and *sodium pyrosulpharsenate*, $Na_4As_2S_7$, are also known. The sulpharsenates of the alkali elements are soluble in water, while those of many elements other than the alkali elements may be made as insoluble colored precipitates.

Arsenides. *Binary compounds of arsenic with positive elements, known as arsenides, may be made in several ways.* Nearly all of the metals will combine directly with arsenic. When arsenic and sodium are gently heated together, *sodium arsenide*, Na_3As, is obtained as a dark solid, acted upon by acids, and arsenides of other metals may be formed in a similar manner.

Some metals form a number of different arsenides. By heating copper and arsenic together, in proper proportions and at the required temperatures, a series of *copper arsenides* may be formed. When arsenious acid, H_3AsO_3, is heated with copper, an arsenide, Cu_5As_2, is deposited as a dark solid. When arsenic is warmed with a solution of a copper salt, such as cupric sulphate, $CuSO_4$, the compound Cu_2As, is formed. By the interaction of arsenic trihydride, AsH_3, and a copper salt, such as cupric chloride, $CuCl_2$, the compound Cu_2As_3 is formed as a black precipitate. Similar arsenides of silver, gold, zinc, lead, and other metals may be made. Many of the arsenides occur native as minerals.

Summary. *Of the arsenic compounds, arsenic trioxide and arsenic pentoxide are both white solids, soluble in water, forming the respective hydroxides — arsenious acid and orthoarsenic acid.*

Arsenious acid, known only in solution, will neutralize bases, forming arsenites, from which metarsenites may be formed by heating. The alkali arsenites are white solids, soluble in water, while the arsenites of many other elements may be formed as characteristic colored precipitates.

By the oxidation of arsenic triaxide, or of arsenic in presence of water, orthoarsenic acid is formed. Orthoarsenic acid may be changed by heating into pyroarsenic acid and metarsenic acid. Orthoarsenic acid will neutralize bases, forming neutral and acid orthoarsenates, from which pyroarsenates and metarsenates may be formed by heating. The alkali arsenates are white solids, soluble in water, while the arsenates of many elements may be formed as characteristic colored precipitates. Orthoarsenic acid and arsenites may be reduced to arsenious acid and arsenites respectively.

Arsenic trihydride, an inflammable, colorless, highly poisonous gas, may be made by the action of hydrogen upon arsenic or arsenic compounds. Arsenic trichloride, a colorless liquid, is made by the combination of arsenic and chlorine, or by the action of hydrochloric acid upon arsenic trioxide. Arsenic trisulphide and arsenic pentasulphide, yellow solids, may be made by fusing arsenic with sulphur, or may be formed as characteristic yellow precipitates. The arsenic sulphides are acted upon by certain sulphides and hydroxides, with the formation of soluble sulpharsenites and arsenites, or sulpharsenates and sulphoxyarsenates. Various insoluble arsenides may be made by the combination of arsenic with positive elements and in other ways.

Antimony, Sb, 120.2

Antimony Ores. Antimony is found in free condition to some extent, but occurs principally combined with sulphur in the mineral *stibnite*, Sb_2S_3. Other sulphides containing antimony in association with arsenic, and combined with copper, silver, lead, iron, and other elements, are known.

Free antimony may be obtained from *stibnite* by roasting the crude sulphide ore with iron,

$$Sb_2S_3 + 3\,Fe = 2\,Sb + 3\,FeS$$

or by oxidizing the ore directly by roasting in an excess of air,

$$2\,Sb_2S_3 + 9\,O_2 = 2\,Sb_2O_3 + 6\,SO_2$$

and reducing the resulting antimony oxide by heating with carbon.

$$Sb_2O_3 + 3\,C = Sb_2 + 3\,CO$$

Antimony sulphide ores may also be reduced by heating with sodium carbonate and charcoal.

$$2\,Sb_2S_3 + 6\,Na_2CO_3 + 12\,C = 2\,Sb_2 + 6\,Na_2S + 18\,CO$$

Antimony. *Antimony* is a silvery white, brittle, crystalline metal, having a specific gravity varying between 6.71 and 6.86, melting at 430°, and vaporizing under ordinary pressure at from 1500° to 1700°. It is unacted upon by dry air at ordinary temperature, but when sufficiently heated takes fire and burns with a blue flame, forming dense white clouds of antimony trioxide. It is slightly tarnished by moist air at atmospheric temperatures, and decomposes water at red heat, forming an oxide. It is attacked by nitric acid and combines directly with chlorine and other elements. Several useful alloys, such as *type metal, pewter* and *white metal*, contain antimony in association with lead, tin, copper, and other metals.

Oxides and Hydroxides. Antimony forms three oxides, and though these oxides do not unite readily with water, there are several hydroxides corresponding to the highest and lowest of the oxides.

OXIDES	HYDROXIDES
Antimony trioxide, Sb_2O_3	Orthoantimonious acid, H_3SbO_3
	Metantimonious acid, $HSbO_2$
Antimony tetroxide, Sb_2O_4	———
Antimony pentoxide, Sb_2O_5	Orthoantimonic acid, H_3SbO_4
	Pyroantimonic acid, $H_4Sb_2O_7$
	Metantimonic acid, $HSbO_3$

From the oxides and related hydroxides of antimony three classes of salts may be derived. From antimony trioxide and the related antimony hydroxides there may be obtained, on the one hand, salts such as $NaSbO_2 \cdot 3\ H_2O$, in which antimony and oxygen constitute the negative ion, and on the other hand, salts such as the sulphates, $Sb_2(SO_4)_3$, $Sb(OH)SO_4$, and the nitrate, $Sb_2(NO_3)_6 \cdot 5\ Sb_2O_3$, in which antimony acts as the positive ion. From antimony pentoxide and the corresponding antimony hydroxides may be obtained salts in which antimony and oxygen constitute the negative ion, as $NaSbO_3$, and $Na_2H_2Sb_2O_7$. All hydroxides of antimony appear therefore to be acidic, while the lower hydroxides, H_3SbO_3 or $Sb(OH)_3$, and $HSbO_2$ or $SbO(OH)$, in which antimony is trivalent, may be basic as well as acidic. Of the antimony oxides antimony trioxide, Sb_2O_3, is acidic or basic according to circumstances, while antimony pentoxide is acidic. When antimony tetroxide is acted upon by reagents, products are formed which may be classed as mixtures of derivatives of antimony trioxide and antimony pentoxide.

Antimony Trioxide. *Antimony trioxide*, Sb_2O_3, a white solid, is formed when antimony is heated in air at a temperature not exceeding 360°. It occurs native in two distinctly different crystalline systems as the minerals *valentinite* and *senarmontite*, and may be prepared artificially in similar forms. When heated out of contact with air it melts at dark red heat and volatilizes without decomposition. At 1560° its specific gravity is about 560, corresponding approximately to the molecular symbol Sb_4O_6, though at this temperature dissociation of the molecule represented by the symbol is apparently beginning. At still higher temperatures antimony trioxide may possibly be represented by the molecular symbol, Sb_2O_3. It is convenient, at all events, to call the oxide antimony trioxide, and to represent it by the equivalent symbol Sb_2O_3.

Heated to a temperature above 590°, in air or oxygen, antimony trioxide is converted completely to antimony tetroxide, Sb_2O_4. It dissolves in water, cold or hot, only slightly, but to a slightly greater degree in cold water. It is little affected by dilute acids, but is attacked by hydrochloric acid with formation of antimonious chloride, and by tartaric acid with formation of antimony tartrate, or antimoniotartaric acid, while strong sulphuric acid acts upon it to form sulphates.

Antimonious Acids. *The normal hydroxide and oxyhydrides of antimony, corresponding to antimony trioxide, have been prepared. Orthoantimonious acid,* H_3SbO_3, the normal antimonious hydroxide, has been isolated by adding sulphuric acid in exactly proper amount to a solution of barium dihydrogen antimoniotartrate, $BaH_2(C_4H_4O_6)_2 \cdot Sb_2O_3$, filtering off the precipitated barium sulphate, adding more sulphuric acid to the clear solution of antimoniotartaric acid, and collecting and drying at 100° the white precipitate which is formed.

$$BaH_2(C_4H_4O_6)_2 \cdot Sb_2O_3 + H_2SO_4 = BaSO_4 + H_4(C_4H_4O_6)_2 \cdot Sb_2O_3$$

$$H_4(C_4H_4O_6)_2 \cdot Sb_2O_3 + 3\,H_2O = 2\,H_3SbO_3 + 2\,H_2(C_4H_4O_6)$$

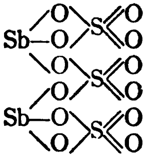
Metantimonious acid, $HSbO_2$, an antimonious oxyhydroxide, has been prepared by a reaction closely similar to that by which orthoantimonious acid has been made, by decomposing potassium dihydrogen antimoniotartrate, $K_2H_2(C_4H_4O_6)_2 \cdot Sb_2O_3$, by certain salts, such as the carbonates, phosphates, and acetates of the alkali metals; while by the action of ammonium hydroxide upon potassium dihydrogen antimoniotartrate, antimony trioxide, Sb_2O_3, the completely dehydrated derivative of orthoantimonious acid, has been precipitated.

Antimonites. *From orthoantimonious acid, metantimonious acid, or antimony trioxide, antimonites of the alkali metals in which antimony is in the negative ion may be prepared.* When the saturated solution obtained by acting upon any one of these substances with a 50 per cent. solution of sodium hydroxide is diluted with hot water, a part of the dissolved material separates from solution and the filtered liquid deposits on cooling crystals of *sodium metantimonite*, $NaSbO_2 \cdot 3\,H_2O$, which may, however, be best regarded as *sodium dihydrogen orthoantimonite*, $NaH_2SbO_3 \cdot 2\,H_2O$. It is not improbable that in the presence of a sufficiency of alkali hydroxides, other sodium orthoantimonites, such as Na_2HSbO_3 and Na_3SbO_3, may exist. Such compounds, however, would be readily hydrolyzed, and have not been isolated.

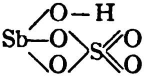
If the saturated solution from which orthoantimonites may be obtained is allowed to cool without dilution, crystalline salts are formed containing a large proportion of antimony. In this way sodium antimonites, represented by the symbols $NaH_2Sb_3O_6$, $Na_4H_2Sb_6O_{12}$, and $NaSb_5O_8$, which may be regarded as derivatives of a polymerized metantimonious acid, have been prepared. Potassium salts, KSb_3O_5, and $KSb_3O_5 \cdot 3\,H_2O$, are also known. The alkali antimonites, which are the sole representatives of the salts of the antimonite series, are all easily hydrolyzed, with separation of antimony trioxide.

Antimony Salts. *Salts in which antimony plays the part of a positive ion may be made by acting upon antimony trioxide with strong sulphuric acid or strong nitric acid.*

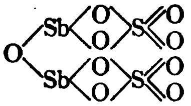
Antimony Sulphate. A neutral *antimony sulphate*, $Sb_2(SO_4)_3$, or



crystallizes from the solution obtained by acting upon antimony trioxide with concentrated sulphuric acid. When, however, antimony trioxide is treated with dilute sulphuric acid of from 50 per cent. to 70 per cent. strength, a basic antimony sulphate, $Sb(OH)SO_4$, or

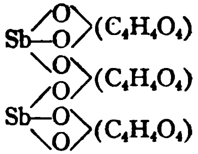


is precipitated. This compound loses water at 100°, giving an antimony oxysulphate, $Sb_2O(SO_4)_2$, or

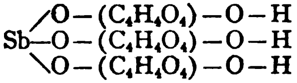


A white crystalline basic *antimony nitrate*, $Sb_2(NO_3)_6 \cdot 5\ Sb_2O_3$, has been formed by the action of strong nitric acid upon antimony trioxide. These salts of antimony, in which antimony is the positive ion, are white crystalline compounds, easily hydrolyzed.

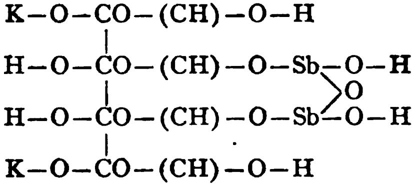
Antimony Tartrates. Tartaric acid, $H_2(C_4H_4O_6)$, as well as other organic acids, is able to act upon antimony trioxide and its related hydroxides. Some of the compounds formed are to be regarded as salts in which antimony is the positive ion, as for example the neutral *antimony tartrate*, $Sb_2(C_4H_4O_6)_3$, or



and an acidic *antimony hydrogen tartrate*, $SbH_3(C_4H_4O_6)_3$, or



On the other hand, it appears to be probable that in certain tartrates of other elements, antimony enters as a constituent of the negative ion. "Tartar emetic," for example, made by acting upon antimony trioxide with potassium hydrogen tartrate, $KH(C_4H_4O_6)$, "cream of tartar," is perhaps best regarded as an acidic *potassium antimoniotartrate*, $K_2H_2(C_4H_4O_6)_2 \cdot Sb_2O_3$, or

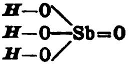


The antimony tartrates and the antimoniotartrates are not so easily hydrolyzed with precipitation of antimony trioxide as are other salts of antimony. Tartar emetic is used as a medicine.

Antimony Tetroxide. *Antimony tetroxide*, Sb_2O_4, a white powder turning yellow when heated, slightly soluble in water, and acted upon with difficulty by acids, may be made by heating antimony trioxide in air or oxygen, the combination of antimony trioxide with oxygen beginning at 360°, and being complete at 590°. It is also made by heating antimony pentoxide, Sb_2O_5, to low redness. When fused with alkali hydroxides or carbonates, antimony tetroxide is acted upon apparently with formation of a mixture of antimonites with antimonates.

Antimony Pentoxide. *Antimony pentoxide*, Sb_2O_5, is a pale yellow powder, obtained by cautiously heating antimony or antimony trioxide with nitric acid, or with aqua regia, or with mercuric oxide, or by heating the antimonic acids. At high temperature it yields oxygen and is converted into antimony tetroxide, the change beginning at 300° in absence of an oxidizing agent. It is very insoluble in water, is slowly attacked by acids, including tartaric acid, and by alkali hydroxides in solution, but is readily attacked by alkali hydroxides in fusion.

Antimonic Acids. *Several antimonic oxyhydroxides, corresponding to antimony pentoxide, are known. Orthoantimonic acid*, H_3SbO_4, an antimonic oxyhydroxide, may be obtained by fusing antimony pentoxide, Sb_2O_5, with three times its weight of potassium hydroxide, decomposing the melt with nitric acid, and drying the precipitate over sulphuric acid, or for a long time in air.



The freshly prepared air-dried precipitate contains an amount of water intermediate between that demanded by the symbols H_5SbO_5 and H_3SbO_4. Although it may be that the normal hydroxide, H_5SbO_5, exists in unstable condition, the oxyhydroxide, H_3SbO_4, is the highest hydroxide found to be stable at ordinary temperature, and bears the name *orthoantimonic acid*.

Orthoantimonic acid may also be formed by the hydrolysis of antimony pentachloride, $SbCl_5$, the product being dried over sulphuric acid,

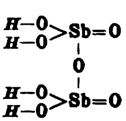
$$SbCl_5 + 4\,H_2O = H_3SbO_4 + 5\,HCl$$

or by treating antimony repeatedly with aqua regia, washing out the product thoroughly with water, and drying over sulphuric acid,

$$6\,Sb + 10\,HNO_3 + 4\,H_2O = 6\,H_3SbO_4 + 10\,NO$$

or by acting with concentrated nitric acid upon antimony trioxide, Sb_2O_3, washing and drying the product similarly.

$$2\,Sb_2O_3 + 4\,HNO_3 + 4\,H_2O = 4\,H_3SbO_4 + 2\,N_2O_3$$

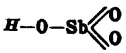


Pyroantimonic acid, $H_4Sb_2O_7$, is formed as a white insoluble substance when orthoantimonic acid, H_3SbO_4, is heated to 100°,

$$2\,H_3SbO_4 = H_4Sb_2O_7 + H_2O$$

or when antimony pentachloride, $SbCl_5$, is hydrolyzed in hot solution.

$$2\,SbCl_5 + 7\,H_2O = H_4Sb_2O_7 + 10\,HCl$$



Metantimonic acid, $HSbO_3$, white and insoluble, is produced by heating orthoantimonic acid, H_3SbO_4, or pyroantimonic acid, $H_4Sb_2O_7$, to 175°.

$$H_3SbO_4 = HSbO_3 + H_2O$$

$$H_4Sb_2O_7 = 2\,HSbO_3 + H_2O$$

At 275° metantimonic acid, $HSbO_3$, yields antimony pentoxide, Sb_2O_5,

$$2\,HSbO_3 = Sb_2O_5 + H_2O$$

which at low redness passes into antimony tetroxide.

$$2\,Sb_2O_5 = Sb_2O_4 + O_2$$

Antimonates.

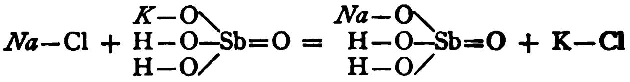
Antimonates of the alkali elements, in which antimony is in the negative ion, may be prepared.

Antimonates of the alkali elements may be made by melting together antimony pentoxide and the alkali hydroxides, or by fusing antimony, antimony trioxide, or other compounds of antimony with an alkali nitrate. From the alkali antimonates, more or less soluble, antimonates of other elements may be precipitated by adding the alkali antimonate to suitable salts of the other elements.

By fusing to redness for some time a mixture of antimony with three or four times its weight of potassium nitrate, a residue is obtained which, after extraction with cold water, yields upon long boiling with water a solution from which an acidic salt, *potassium dihydrogen orthoantimonate*, is left upon evaporation. This salt is obtained as a gummy mass which, when dried at 100°, has the composition expressed by the symbol $KH_2SbO_4 \cdot 2\,H_2O$, but which at 185° exists in the anhydrous form, KH_2SbO_4.

From the solution of this salt in water, carbon dioxide precipitates a derivative of a polymeric antimonic acid which, when dried at 100°, has the composition represented by the symbol $2\,K_2H_5Sb_2O_8$.

From solutions of sodium salts, potassium dihydrogen antimonate precipitates the white crystalline, difficultly soluble, acidic *sodium dihydrogen orthoantimonate*, $NaH_2SbO_4 \cdot 2\,H_2O$.



$$\mathit{Na}{-}\mathrm{Cl} + \begin{array}{l}\mathit{K}{-}\mathrm{O}\diagdown \\ \mathrm{H{-}O{-}Sb{=}O} \\ \mathrm{H{-}O}\diagup\end{array} = \begin{array}{l}\mathit{Na}{-}\mathrm{O}\diagdown \\ \mathrm{H{-}O{-}Sb{=}O} \\ \mathrm{H{-}O}\diagup\end{array} + \mathrm{K{-}Cl}$$

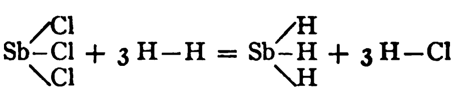
Other antimonates, such as $LiH_2SbO_4 \cdot 2\,H_2O$, $AgH_2SbO_4 \cdot 2\,H_2O$, and $HgH_4Sb_2O_8 \cdot 4\,H_2O$ have been similarly formed by precipitation.

Both potassium dihydrogen orthoantimonate and sodium dihydrogen orthoantimonate yield, when heated to 350°, acidic *pyroantimonates* of the composition $K_2H_2Sb_2O_7$ and $Na_2H_2Sb_2O_7$ respectively.

All of the orthoantimonates that have been mentioned are of the prevailing acidic type containing one atom of the metal in the molecule. It may be that neutral antimonates containing three atoms of the alkali metal in the molecule may be formed when antimony pentoxide is fused with an excess of alkali hydroxide, but if so, such salts do not survive hydrolytic action in solution. From the antimonates by the action of stronger acids orthoantimonic acid is formed more or less completely.

Binary Antimony Compounds. *Antimony forms with hydrogen and chlorine and other elements various binary compounds.*

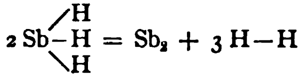
Antimony Trihydride. *Antimony trihydride*, SbH_3 (stibine), ordinarily a colorless gas, is best prepared approximately pure by the action of strong acids upon an alloy of antimony, and it is also formed when nascent hydrogen acts upon a soluble compound of antimony, such as antimony trichloride, $SbCl_3$, in the presence of an acid.



$$\mathrm{Sb}\begin{array}{l}\diagup\mathrm{Cl} \\ {-}\mathrm{Cl} \\ \diagdown\mathrm{Cl}\end{array} + 3\,\mathrm{H{-}H} = \mathrm{Sb}\begin{array}{l}\diagup\mathrm{H} \\ {-}\mathrm{H} \\ \diagdown\mathrm{H}\end{array} + 3\,\mathrm{H{-}Cl}$$

Even under the most favorable circumstances of production, however, antimony trihydride is always accompanied by hydrogen.

When obtained in pure condition by reducing it to solid form by cold and pressure, antimony trihydride melts at −91.5° and boils at −18°. It is slightly soluble in water, possesses a characteristic odor and unpleasant taste, and is poisonous. It burns in air with formation of antimony trioxide and water. It is easily dissociated with hydrogen and antimony, the action beginning at low temperatures and becoming complete when the gas is passed through a glass tube heated to low redness.

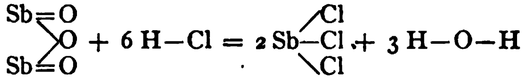


$$2\,\mathrm{Sb}\begin{matrix}\diagup \mathrm{H}\\ -\mathrm{H}\\ \diagdown \mathrm{H}\end{matrix} = \mathrm{Sb_2} + 3\,\mathrm{H{-}H}$$

Marsh Test for Antimony Compounds. Very small amounts of antimony compounds respond to the *Marsh test* when introduced into the hydrogen generator, containing zinc and sulphuric acid or hydrochloric acid. The black antimony mirror formed when the mixture of hydrogen and antimony hydride is ignited and allowed to impinge upon cold porcelain or when the mixture of the gas is passed through a hot tube is, however, distinguishable from the arsenic mirror by the failure of sodium hypochlorite to act upon it appreciably and immediately.

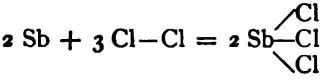
Antimony Chlorides. *Antimony forms two sets of compounds with chlorine and similar elements, and with sulphur.*

Antimony trichloride, $SbCl_3$, is a crystalline solid, soft and deliquescent, melting at 73°, boiling at 223°. It may be prepared by acting upon antimony trioxide, Sb_2O_3, with strong hydrochloric acid, and evaporating the solution,



$$\begin{matrix}\mathrm{Sb{=}O}\\ \rangle \mathrm{O}\\ \mathrm{Sb{=}O}\end{matrix} + 6\,\mathrm{H{-}Cl} = 2\,\mathrm{Sb}\begin{matrix}\diagup \mathrm{Cl}\\ -\mathrm{Cl}\\ \diagdown \mathrm{Cl}\end{matrix} + 3\,\mathrm{H{-}O{-}H}$$

or by acting with chlorine upon an excess of antimony.



$$2\,\mathrm{Sb} + 3\,\mathrm{Cl{-}Cl} = 2\,\mathrm{Sb}\begin{matrix}\diagup \mathrm{Cl}\\ -\mathrm{Cl}\\ \diagdown \mathrm{Cl}\end{matrix}$$

Water in very small amount, not exceeding the proportion of two equivalents of water to one equivalent of the salt, dissolves antimony trichloride. More water forms a basic chloride, $Sb_4O_4Cl_4$, and still more water gives the basic chloride, $Sb_4O_5Cl_2$. The simple basic chloride, SbOCl, is formed when alcohol acts upon antimony trichloride.

Antimony pentachloride, $SbCl_5$, a yellow liquid readily frozen to crystals which melt at −6°, is made by acting upon antimony with an excess of chlorine.

$$2\,\mathrm{Sb} + 5\,\mathrm{Cl_2} = 2\,\mathrm{SbCl_5}$$

It is easily dissociated into chlorine and antimony trichloride. With a suitable amount of water, crystalline compounds, $SbCl_5 \cdot H_2O$ and

$SbCl_5 \cdot 4\,H_2O$, are formed, but an excess of water hydrolyzes antimony pentachloride to orthoantimonic acid, H_3SbO_4, or pyroantimonic acid, $H_4Sb_2O_7$.

Antimony tribromide, $SbBr_3$, white and crystalline; *antimony triiodide*, SbI_3, a red crystalline compound; and *antimony pentaiodide*, SbI_5, dark brown and crystalline, are salts easily hydrolyzed by water. *Antimony trifluoride*, SbF_3, and *antimony pentafluoride*, SbF_5, are also known.

Antimony trichloride, *antimony tribromide*, *antimony triiodide*, and *antimony trifluoride* form double salts with halogen salts of the alkali elements in great variety. For example we have $4\,NH_4I \cdot SbI_3 \cdot 3\,H_2O$, $7\,KCl \cdot 3\,SbCl_3$, $3\,RbBr \cdot 2\,SbBr_3$, $3\,NH_4I \cdot 4\,SbI_3 \cdot 9\,H_2O$, $RbCl \cdot 2\,SbCl_3$, $3\,NaCl \cdot SbCl_3$, $2\,KCl \cdot SbCl_3$, $KF \cdot SbF_3$, $4\,CsF \cdot 7\,SbF_3$, $CsF \cdot SbF_3$, etc.

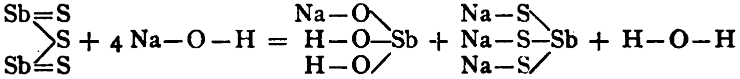
Antimony Trisulphide. *Antimony trisulphide*, Sb_2S_3 (antimonious sulphide), found native as the mineral *stibnite*, is a dark gray crystalline solid, of specific gravity 4.7, insoluble in water. It is an ore of antimony. It may be made artificially by heating together antimony and sulphur in proper proportions. An orange-red variety of antimony sulphide may be formed as a precipitate by passing hydrogen sulphide through a solution of antimony trichloride, $SbCl_3$, or other soluble antimonious compound in presence of an acid.

$$2\,SbCl_3 + 3\,H_2S = Sb_2S_3 + 6\,HCl$$

When ammonium sulphide, $(NH_4)_2S$, is added to the solution of an antimonious salt, antimonious trisulphide, Sb_2S_3, is first precipitated, and then acted upon by the excess of ammonium sulphide, to form a soluble product.

By heating above 200°, the red antimony trisulphide may be changed into the gray crystalline variety. Heated in air or oxygen, antimony trisulphide is oxidized to antimony trioxide, Sb_2O_3, and sulphur dioxide. Ignited in an atmosphere of steam, antimony trisulphide is converted to *antimony cinnabar*, a red pigment having the composition Sb_2S_2O, which is also found as a mineral. By acting upon antimony trisulphide with concentrated hydrochloric acid, antimony trichloride, $SbCl_3$, and hydrogen sulphide are formed.

Sulph-antimonites. The precipitate of antimony trisulphide is acted upon by alkali hydroxides with formation of soluble *antimonites* and *sulphantimonites* of unknown composition. Thus, in the action of sodium hydroxide upon antimony trisulphide, Sb_2S_3, it may be supposed that sodium dihydrogen orthoantimonite, NaH_2SbO_3, and *sodium sulphantimonite*, Na_3SbS_3, a substance like the known sodium sulpharsenite, are formed, and remain in solution.



$$\begin{array}{l}Sb{=}S\\ \quad\rangle S\\ Sb{=}S\end{array} + 4\,Na{-}O{-}H = \begin{array}{l}Na{-}O\diagdown\\ H{-}O{-}Sb\\ H{-}O\diagup\end{array} + \begin{array}{l}Na{-}S\diagdown\\ Na{-}S{-}Sb\\ Na{-}S\diagup\end{array} + H{-}O{-}H$$

Ammonium sulphide, $(NH_4)_2S$, acts similarly upon precipitated antimony trisulphide, Sb_2S_3. to form in solution products like *ammonium sulphantimonite*, $(NH_4)_3SbS_3$.

The soluble sulphantimonites are decomposed by acids, with precipitation of antimony trisulphide and formation of hydrogen sulphide. If to a solution containing sodium sulphantimonite, Na_3SbS_3, we add hydrochloric acid, antimony trisulphide, Sb_2S_3, is precipitated, and hydrogen sulphide is evolved.

$$2\,Na_3SbS_3 + 6\,HCl = Sb_2S_3 + 3\,H_2S + 6\,NaCl$$

Antimony Pentasulphide. *Antimony pentasulphide*, Sb_2S_5, a powder of orange color, is not found in native state, but is made artificially by adding hydrogen sulphide to solutions of antimonic compounds, or by acting upon the sulphantimonates with hydrochloric acid. It is precipitated by hydrogen sulphide, H_2S, from a cold solution made by dissolving antimony pentachloride, $SbCl_5$, in dilute hydrochloric acid.

$$2\,SbCl_5 + 5\,H_2S = Sb_2S_5 + 10\,HCl$$

In warm solution antimony pentasulphide tends to decompose into antimony trisulphide, Sb_2S_3, and sulphur, and the dry substance is decomposed similarly when heated. Acted upon by hydrochloric acid, it is converted to antimony trisulphide and sulphur, and by sufficiently strong acid into antimony trichloride, sulphur, and hydrogen sulphide.

When ammonium sulphide, $(NH_4)_2S$, is added to a solution of an antimonic salt, in the presence of an acid, antimony pentasulphide, Sb_2S_5, is first precipitated, and is then acted upon by an excess of ammonium sulphide with formation of a soluble product.

Sulphantimonates. The precipitate of antimony pentasulphide is acted upon by alkali hydroxides, with formation of antimonates and sulphantimonates of the alkali elements, which by the action of acids are decomposed, with formation of antimony pentasulphide. By acting upon antimony pentasulphide, Sb_2S_5, with sodium hydroxide, insoluble sodium dihydrogen orthoantimonate, NaH_2SbO_4, and soluble *sodium sulphantimonate*, Na_3SbS_4, may be formed.

$$4\,Sb_2S_5 + 18\,NaOH = 3\,NaH_2SbO_4 + 5\,Na_3SbS_4 + 6\,H_2O$$

An excess of sodium hydroxide acts upon the insoluble sodium antimonate with formation of a solution containing probably a less acidic sodium antimonate and sodium sulphantimonate. From this solution hydrochloric acid precipitates antimony pentasulphide, Sb_2S_5. The action of an alkali hydroxide upon antimony pentasulphide may also result in the formation of a sulphoxyantimonate, such as the *potassium sulphoxyantimonate*, $K_2HSbSO_3 \cdot 2\,H_2O$, for example.

Ammonium sulphide, $(NH_4)_2S$, acts upon precipitated antimony pentasulphide, Sb_2S_5, with formation of *ammonium sulphantimonate*, $(NH_4)_3SbS_4$, which is decomposed by acids, with formation of antimony pentasulphide, or antimony trisulphide and sulphur.

Metasulphantimonates, such as $NaSbS_2$, are also known, as well as more complex compounds of similar composition, and these may be made by direct combination of antimony trisulphide, Sb_2S_3, with sulphides of other elements, either by fusing the substances together, or by mixing their solutions.

The sulphantimonates may be prepared in various ways, many of them being formed as colored insoluble precipitates. *Sodium sulphantimonates*, $Na_3SbS_4 \cdot 9\,H_2O$, known as *Schlippe's salt*, may be formed as large yellow crystals, by boiling antimony trisulphide with sulphur and sodium hydroxide. Some of the sulphantimonates occur as minerals.

Summary. *Antimony trioxide may be made by burning antimony in air at a suitably low temperature; antimony tetroxide is obtained by strongly heating the antimony trioxide in air, or by heating antimony pentoxide above its point of dissociation; antimony pentoxide may be made by suitably heating antimony or antimony trioxide with more active oxidizers.*

Orthoantimonious acid and metantimonious acid have been prepared by the action of certain acids or salts upon suitable compounds of antimony. Orthoantimonic acid, pyroantimonic acid, and metantimonic acid are formed in successive stages by dehydrating the product obtained when antimony pentoxide is fused with potassium hydroxide and the melt is treated with nitric acid.

By acting upon antimony trioxide with sodium hydroxide, sodium metantimonites are formed; by fusing antimony with potassium nitrate, and extracting the mass with water, potassium dihydrogen orthoantimonate may be formed. Antimony trioxide may be acted upon by sulphuric *acid to form antimony sulphates which are readily hydrolyzed by water, and a basic antimony nitrate is also definitely known.*

Antimony trihydride, a colorless gas, made by acting upon soluble compounds of antimony with nascent hydrogen, burns in air to form antimony trioxide, and when heated dissociates into antimony and hydrogen.

Antimony trichloride may be made by acting upon antimony trioxide with hydrochloric acid, and by the direct combination of antimony with chlorine, and is decomposed by water with formation of antimony oxychlorides. Antimony pentachloride may be made by acting upon antimony trichloride with chlorine. Antimony bromides and iodides may be similarly formed.

Antimony trisulphide and antimony pentasulphide may be formed as precipitates by the action of hydrogen sulphide in presence of an acid upon antimonious compounds in solution, and are acted upon by sodium sulphide or by ammonium sulphide with the formation of soluble sulphantimonites and sulphantimonates respectively, which are decomposed by acids with formation of the corresponding antimony sulphides.

Bismuth, Bi, 208.5

Bismuth. Bismuth, a comparatively rare element, is found chiefly uncombined, sometimes in pure condition, but more frequently mixed with small amounts of other metals, from which it may be separated by melting at low temperatures. It is also found combined in certain rare minerals, such as *bismuth ochre*, Bi_2O_3, and *bismuthinite*, Bi_2S_3, from which bismuth may be obtained by treatment with hydrochloric acid, and reduction of the resulting basic bismuth chloride with carbon in the presence of a suitable flux.

Bismuth is a reddish white metal of specific gravity 9.9, and very brittle. It may be melted at 265°, and at about 1300° it boils, forming a vapor of specific gravity about 320 intermediate between the values corresponding to the molecular symbols Bi and Bi_2. The molten metal expands slightly on cooling and tends to form crystals, which may be obtained by breaking the superficial crust which forms before the metal solidifies entirely, and pouring out the molten interior. Bismuth is but little affected by air or by water at the ordinary temperature, but when strongly heated burns in air, and at high temperatures slowly decomposes steam. It is attacked by nitric acid and by hot sulphuric acid, but is unaffected by hydrochloric acid. It combines directly with chlorine and similar elements.

Alloys. Bismuth forms with lead, tin, and cadmium, alloys which melt at low temperatures. *Rose's metal,* which is composed of 2 parts bismuth, 1 part lead, and 1 part tin, melts at 93.7°, and *Wood's metal,* 4 parts bismuth, 2 parts lead, 1 part tin, 1 part cadmium, melts at 60.5°, both melting below the temperature of boiling water. Several such *fusible metals* are employed as solders, and as safety plugs for boilers and for automatic sprinklers. Bismuth alloys are also, by reason of their slight expansion in volume on cooling, useful in *stereotyping.* Joined to antimony, bismuth forms a *thermo-electric couple* exceedingly sensitive to a slight variation of temperature at their point of juncture. The compounds of bismuth are used in making cosmetics and medicinal preparations.

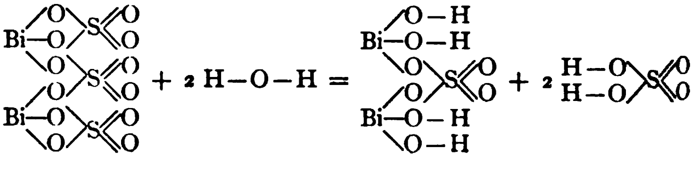
Bismuth Salts. *Bismuth is capable of forming some salts in which it is a positive ion.*

Bismuth Sulphates. When bismuth is heated with concentrated sulphuric acid, sulphur dioxide is evolved, and the evaporation of the excess of acid leaves a white amorphous mass of normal *bismuth sulphate,* $Bi_2(SO_4)_3$.

$$2\ Bi + 6\ H_2SO_4 = Bi_2(SO_4)_3 + 6\ H_2O + 3\ SO_2$$

By the combination of bismuth sulphate with a small amount of water, crystals of hydrated salts may be obtained of which $Bi_2(SO_4)_3 \cdot 3\ H_2O$ may serve as an example.

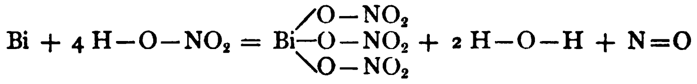
With large amounts of water, bismuth sulphate undergoes hydrolytic decomposition, with formation of a basic bismuth sulphate, of which several have been obtained. Thus water acts upon normal bismuth sulphate, $Bi_2(SO_4)_3$ to form a basic *bismuth hydroxysulphate* of the composition $Bi_2(OH)_4SO_4$.



This salt, upon heating, loses water with formation of an oxysalt, $Bi_2O_2(SO_4)$, which, when strongly heated, evolves sulphur trioxide, and is converted to bismuth trioxide.

The normal and basic bismuth sulphates may also be obtained by acting upon bismuth trioxide with sulphuric acid.

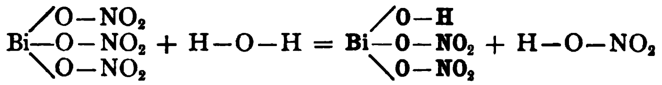
Bismuth Nitrates. When bismuth is acted upon by nitric acid, a solution is formed from which neutral *bismuth nitrate*, $Bi(NO_3)_3 \cdot 5\,H_2O$, may be obtained as white crystals,



$$\mathrm{Bi} + 4\,\mathrm{H{-}O{-}NO_2} = \mathrm{Bi}\begin{matrix}/\mathrm{O{-}NO_2}\\ -\mathrm{O{-}NO_2}\\ \backslash \mathrm{O{-}NO_2}\end{matrix} + 2\,\mathrm{H{-}O{-}H} + \mathrm{N{=}O}$$

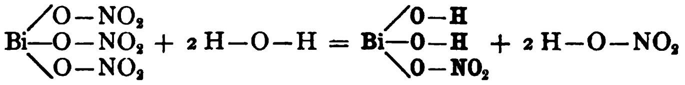
and the same compound may be obtained by acting upon bismuth trioxide with nitric acid.

The neutral bismuth nitrate may be dissolved in a suitably small amount of water, but more water forms an insoluble basic salt. Water acts upon bismuth nitrate, $Bi(NO_3)_3$, according to proportions, to form *bismuth hydroxynitrate*, $Bi(OH)(NO_3)_2$,



$$\mathrm{Bi}\begin{matrix}/\mathrm{O{-}NO_2}\\ -\mathrm{O{-}NO_2}\\ \backslash \mathrm{O{-}NO_2}\end{matrix} + \mathrm{H{-}O{-}H} = \mathrm{Bi}\begin{matrix}/\mathrm{O{-}H}\\ -\mathrm{O{-}NO_2}\\ \backslash \mathrm{O{-}NO_2}\end{matrix} + \mathrm{H{-}O{-}NO_2}$$

or *bismuth dihydroxynitrate*, $Bi(OH)_2NO_3$,



$$\mathrm{Bi}\begin{matrix}/\mathrm{O{-}NO_2}\\ -\mathrm{O{-}NO_2}\\ \backslash \mathrm{O{-}NO_2}\end{matrix} + 2\,\mathrm{H{-}O{-}H} = \mathrm{Bi}\begin{matrix}/\mathrm{O{-}H}\\ -\mathrm{O{-}H}\\ \backslash \mathrm{O{-}NO_2}\end{matrix} + 2\,\mathrm{H{-}O{-}NO_2}$$

or other salts still more basic and more nearly approaching the composition of bismuth hydroxide. Upon heating, the basic bismuth hydroxynitrates evolve water, tending to form oxysalts, which in turn are decomposed by further heating until bismuth trioxide remains.

When a few drops of clear solution of bismuth nitrate, $Bi(NO_3)_3$, such as may be obtained by acting upon bismuth nitrate with nitric acid, are poured into a large mass of water, if the solution does not contain too much free acid, basic bismuth hydroxynitrate may form as a white precipitate, which may be acted upon by a suitable amount of nitric acid.

When crystallized neutral bismuth nitrate is heated it is hydrolyzed by its own water of crystallization forming hydroxysalts or oxysalts. The compounds $BiOH(NO_3)_2$, $Bi(OH)_2NO_3$, $BiO(NO_3)$, as well as others of similar constitution, may be obtained in this manner. The white insoluble powder largely used in medicine under the name ***bismuth subnitrate*** consists of the compounds $Bi(OH)_2NO_3$ and $Bi(OH)(NO_3)_2$.

Insoluble Bismuth Salts. *Some bismuth salts may be formed as precipitates by adding suitable reagents to solutions of bismuth compounds.* When we add a solution of sodium carbonate, or other carbonate, to a solution of bismuth nitrate, $Bi(NO_3)_3$, a white precipitate of a basic ***bismuth carbonate,*** of composition varying with the conditions, is formed, which is acted upon by acids, and decomposed by heating, with formation of bismuth trioxide. The salt ordinarily precipitated by sodium carbonate from cold solutions has the composition $Bi_4(OH)_2O_3(CO_3)_2$.

$$4\,Bi(NO_3)_3 + 6\,Na_2CO_3 + H_2O = Bi_4(OH)_2O_3(CO_3)_2 + 12\,NaNO_3 + 4\,CO_2$$

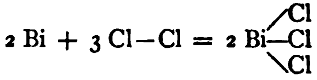
When potassium chromate, K_2CrO_4, or other soluble chromate, is added to a solution of bismuth nitrate, a yellow precipitate of basic *bismuth chromate,* $Bi_2O(CrO_4)_2$, is formed, and this is acted upon by dilute nitric acid.

$$2\,Bi(NO_3)_3 + 3\,K_2CrO_4 + H_2O = Bi_2O(CrO_4)_2 + 6\,KNO_3 + H_2CrO_4$$

Among other bismuth salts which may be formed are ***bismuth orthophosphate,*** $BiPO_4$, *bismuth orthoarsenate,* $BiAsO_4$, ***bismuth orthoantimonate,*** $BiSbO_4$, and corresponding oxysalts.

Binary Bismuth Compounds. *Bismuth combines directly with chlorine and similar elements and with sulphur to form binary compounds.*

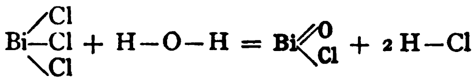
When bismuth is heated in a stream of chlorine, ***bismuth trichloride,*** $BiCl_3$, is formed as a white crystalline mass, melting at 220°, and boiling at about 447°.



$$2\,Bi + 3\,Cl{-}Cl = 2\,Bi{<}\begin{matrix}Cl\\Cl\\Cl\end{matrix}$$

Bismuth trichloride forms many double compounds, as, for example, $4\,NH_4Cl \cdot BiCl_3$, $3\,KCl \cdot BiCl_3$, etc. From the residue left after evaporating the water from solutions formed by acting upon bismuth trioxide with hydrochloric acid, bismuth trichloride may be distilled, and from the solution containing hydrochloric acid the hydrated compound, $2\,BiCl_3 \cdot HCl \cdot 3\,H_2O$, may be obtained.

Water acts upon bismuth trichloride to form bismuth oxychloride, BiOCl, a white precipitate.

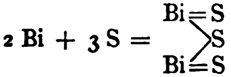


$$Bi\begin{matrix} /Cl \\ -Cl \\ \backslash Cl \end{matrix} + H-O-H = \mathbf{Bi}\begin{matrix} /O \\ \backslash Cl \end{matrix} + 2\,H-Cl$$

The formation of this insoluble basic chloride by diluting with water the hydrochloric acid solution containing bismuth is one of the analytical tests frequently employed in identifying bismuth compounds.

Bismuth tribromide, $BiBr_3$, *bismuth triiodide*, BiI_3, and *bismuth trifluoride*, BiF_3, and corresponding oxysalts and double salts, are also known.

When bismuth is heated with suitable proportions of sulphur, *bismuth trisulphide*, Bi_2S_3, may be formed as a dark crystalline mass.



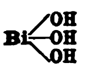
$$2\,Bi + 3\,S = \begin{matrix} Bi=S \\ \quad >S \\ Bi=S \end{matrix}$$

Bismuth trisulphide may also be formed as a black precipitate by adding hydrogen sulphide or other soluble sulphide to a solution of bismuth trichloride, $BiCl_3$, or other bismuth compound.

$$2\,BiCl_3 + 3\,H_2S = \mathbf{Bi_2S_3} + 6\,HCl$$

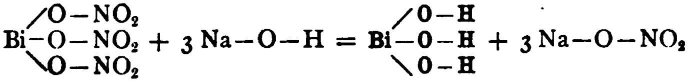
The precipitate is acted upon by boiling nitric acid with formation of bismuth nitrate, and when strongly heated in the air it is oxidized with formation of bismuth trioxide. Bismuth trisulphide is found native as *bismuthinite*, a crystallized mineral.

Hydroxides and Oxides. *The hydroxides and oxides of bismuth may be made from the bismuth salts.*



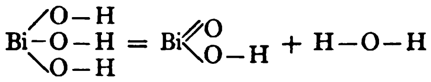
$$\mathbf{Bi}\begin{matrix} /OH \\ -OH \\ \backslash OH \end{matrix}$$

When sodium hydroxide or any other soluble basic hydroxide is added to a solution of bismuth nitrate, $Bi(NO_3)_3$, or bismuth trichloride, $BiCl_3$, or other bismuth compound, a white flocky precipitate is formed, which is probably for the most part *bismuth hydroxide*, $Bi(OH)_3$, contaminated somewhat with a basic salt. The contaminating basic salt of bismuth is present to a less degree when, in forming the hydroxide, the bismuth salt is added in solution to an excess of alkali hydroxide and the excess of this neutralized by cautious additions of an acid.



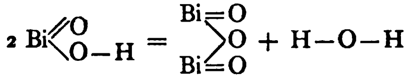
$$Bi\begin{matrix} /O-NO_2 \\ -O-NO_2 \\ \backslash O-NO_2 \end{matrix} + 3\,Na-O-H = \mathbf{Bi}\begin{matrix} /\mathbf{O-H} \\ -\mathbf{O-H} \\ \backslash \mathbf{O-H} \end{matrix} + 3\,Na-O-NO_2$$

When the flocky precipitate of bismuth hydroxide, $Bi(OH)_3$, is dried at 100°, a white insoluble residue of *bismuth oxyhydroxide*, $BiO(OH)$, remains,



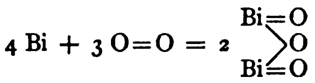
$$\mathrm{Bi}\left\langle\begin{matrix}\mathrm{O-H}\\ \mathrm{O-H}\\ \mathrm{O-H}\end{matrix}\right. = \mathrm{Bi}\left\langle\begin{matrix}\mathrm{O}\\ \mathrm{O-H}\end{matrix}\right. + \mathrm{H-O-H}$$

which, upon further heating, evolves water, forming *bismuth trioxide*, Bi_2O_3.



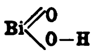
$$2\,\mathrm{Bi}\left\langle\begin{matrix}\mathrm{O}\\ \mathrm{O-H}\end{matrix}\right. = \begin{matrix}\mathrm{Bi=O}\\ \rangle\mathrm{O}\\ \mathrm{Bi=O}\end{matrix} + \mathrm{H-O-H}$$

Bismuth trioxide may also be formed by heating bismuth in air.



$$4\,\mathrm{Bi} + 3\,\mathrm{O=O} = 2\begin{matrix}\mathrm{Bi=O}\\ \rangle\mathrm{O}\\ \mathrm{Bi=O}\end{matrix}$$

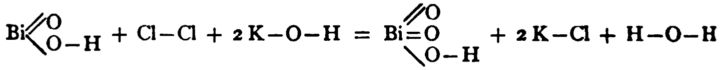
When bismuth hydroxide, $Bi(OH)_3$, is precipitated in the presence of a suitable reducing agent, such as sodium stannate, part of the bismuth hydroxide is reduced to bismuth.



$$\mathrm{Bi}\left\langle\begin{matrix}\mathrm{O}\\ \mathrm{O-H}\end{matrix}\right.$$

Bismuth oxyhydroxide, $BiO(OH)$, is an insoluble white powder, unacted upon by basic hydroxides. *Bismuth trioxide*, Bi_2O_3, is a yellow powder of specific gravity 8.2, insoluble in water, unacted upon by basic hydroxides. It occurs naturally as a mineral *bismuth ochre*, and is made artificially by heating bismuth nitrate, or other bismuth compounds, and also by roasting the bismuth ores. The flocky bismuth hydroxide and the powdery bismuth oxyhydroxide and bismuth trioxide are acted upon by strong acids, such as sulphuric acid, nitric acid, and hydrochloric acid, with formation of the corresponding bismuth salts.

Bismuthic oxyhydroxide, $BiO_2(OH)$ (bismuthic acid), may be obtained as a red powder by passing chlorine into a hot solution of potassium hydroxide containing bismuth oxyhydroxide, $BiO(OH)$, or bismuth trioxide, Bi_2O_3, in suspension, and acting upon the residue with dilute nitric acid.

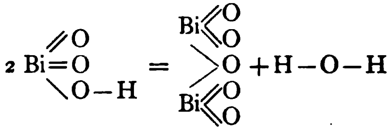


$$\mathrm{Bi}\left\langle\begin{matrix}\mathrm{O}\\ \mathrm{O-H}\end{matrix}\right. + \mathrm{Cl-Cl} + 2\,\mathrm{K-O-H} = \mathrm{Bi}\begin{matrix}\diagup\!\!\mathrm{O}\\ \mathrm{=O}\\ \diagdown\mathrm{O-H}\end{matrix} + 2\,\mathrm{K-Cl} + \mathrm{H-O-H}$$

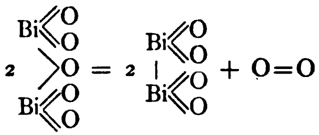
It may also be made by fusing bismuth basic nitrates with potassium hydroxide in presence of air, and acting upon the residue with water and with dilute nitric acid.

The action upon bismuth oxyhydroxide of suitable oxidizers, such as chlorine, in presence of alkali hydroxides, appears in the processes described to form at first unstable and indefinite alkali salts of bismuthic acid, which, if they actually exist, are easily decomposed.

Bismuthic oxyhydroxide, $BiO_2(OH)$, when heated to 120°, loses water and is converted to *bismuth pentoxide*, Bi_2O_5, a brown powder,



and at 225° bismuth pentoxide, Bi_2O_5, evolves oxygen and yields brown *bismuth tetroxide*, Bi_2O_4,



which on further heating evolves more oxygen, forming bismuth trioxide.

Bismuth pentoxide and bismuth tetroxide are both acted upon by sulphuric acid and by hydrochloric acid, with evolution of chlorine.

The existence of unstable bismuth compounds of lower valence corresponding to the symbols Bi_2Cl_4, Bi_2S_2, and Bi_2O_2, has been both affirmed and denied, such compounds having characteristics which might be attributed to mixtures of finely divided metallic bismuth with the familiar bismuth trichloride, BCl_3, bismuth trisulphide, Bi_2S_3, and bismuth trioxide, Bi_2O_3.

Summary. *Bismuth may be acted upon by strong acids with formation of salts, which are very readily changed into insoluble basic compounds by action of water; some bismuth salts may be made as insoluble precipitates; bismuth combines with chlorine to form chlorides, which are changed by water to insoluble basic chlorides; insoluble bismuth trisulphide may be formed by combination of bismuth with sulphur or by precipitation from solutions of bismuth salts.*

By the action of basic hydroxides upon solutions of bismuth salts, bismuth hydroxide is precipitated, and when heated, yields bismuth oxyhydroxide or bismuth trioxide, both insoluble; bismuth trioxide may also be formed by burning bismuth in air; by the action of reducing agents flocky bismuth hydroxide may be partially reduced to metallic bismuth; and by oxidizing bismuth oxyhydroxide or bismuth trioxide in presence of an alkali hydroxide, bismuthic oxyhydroxide is obtained, which upon heating gives bismuth pentoxide, bismuth tetroxide, and bismuth trioxide, successively.

CHAPTER IX

PRIMARY SERIES — GROUP VI

Oxygen, O, 16.00

Sulphur, S, 32.06

SELENIUM, Se, 79.2

TELLURIUM, Te, [127.6]

Group VI.

THE elements of the sixth group of the primary series occur both free and combined as widely distributed constituents of our earth.

Oxygen and the Atmosphere.

Oxygen, in free condition, forms about one fifth part by volume of our *atmosphere*, while in combination it forms about eight ninths part by weight of the *ocean* and other bodies of water, and enters largely into the composition of most rocks, particularly the silicates and the carbonates, and the oxides of the various metals. It has been estimated that oxygen comprises nearly one half the weight of the earth's solid crust. Sulphur, in free condition, is found crystallized in certain volcanic regions, while its salts — principally the *sulphates* — and its binary compounds with the common elements known as *sulphides*, constitute many common minerals. The principal natural sulphate is *gypsum*, $CaSO_4 \cdot 2\ H_2O$, found in large areas, while *pyrite*, FeS_2, is the most common of the natural sulphides. Both oxygen and sulphur are found in animals and plants, oxygen in water and all carbohydrates and proteids, and sulphur in some proteids and similar bodies. Selenium and tellurium are found native in very small amounts, usually associated with sulphides. Certain binary compounds of selenium and tellurium with other elements constitute a few rare minerals.

Oxygen is a colorless, odorless gas, supporting the combustion of many substances, and combining with all other elements except fluorine. An allotropic modification of oxygen, known as *ozone*, more active than ordinary oxygen, may be made in various ways, and is readily changed into ordinary oxygen. Oxygen is the most electro-negative of the elements, and forms stable *oxides* with electro-positive and with electro-negative elements. From the oxides many *hydroxides* may be made directly, while some are made only indirectly; the lower oxides of electro-positive elements are basic, while those of electro-negative elements, as well as some higher hydroxides of positive elements, are acidic. Oxygen generally is a constituent of the negative ion in acids, bases, and salts.

Sulphur. Sulphur, ordinarily a pale yellow crystalline solid, is known also as a soft, yellowish brown, amorphous solid, and in certain other rarer allotropic forms. All forms of sulphur are insoluble in water. Sulphur dioxide, SO_2, formed by burning sulphur in air or oxygen, dissolves in water, forming the solution known as *sulphurous acid*, H_2SO_3, which forms with bases the salts known as *sulphites*. Sulphur trioxide, SO_3, found by oxidizing sulphur dioxide, combines with water, forming *sulphuric acid*, H_2SO_4, one of the strongest known acids, which forms with bases the salts known as *sulphates*. In these, and still other hydroxides and salts, sulphur is a constituent of the negative ion. Sulphur also forms binary compounds, known as *sulphides*, by the direct combination of sulphur with positive elements, and also by the replacement of the hydrogen in hydrogen sulphide, H_2S, by positive elements. Other binary compounds of sulphur with more electro-negative elements, such as the sulphur chlorides, may be made by direct combination of sulphur with elements and in other ways.

Selenium and tellurium, in their chemical relations, are very similar to sulphur. They form oxides and hydroxides which exhibit acidic properties, forming with bases salts in which selenium and tellurium, respectively, are electro-negative. Tellurium hydroxide shows a slight tendency to act as a base. The binary compounds of selenium and tellurium are similar to the analogous sulphur compounds.

The prevailing valence of the elements in the third group is IV and VI, and sometimes a valence of II is exhibited.

Oxygen, O, 16.00

Properties of Oxygen. *Oxygen*, discovered by Priestley, in England, in 1774, and by Scheele, in Sweden, in 1775, occurs free in atmospheric air, of which it forms about one fifth part by volume. It is a colorless, odorless gas, of specific gravity 15.90, slightly soluble in water, somewhat more soluble in alcohol. One liter of oxygen, at 0°

and 760 mm. pressure, weighs 1.4291 grm. Its critical temperature is − 118°, and its critical pressure is 50 atmospheres. Liquid oxygen, of bright blue color, at − 118° has a specific gravity of 0.65, and under 1 atmosphere pressure boils at − 184°. Oxygen has also been obtained as a snow-white solid. It is strongly electro-negative, and combines readily with most of the other elements, and may be made to combine with all elements individually excepting fluorine, bromine, and the inert atmospheric elements. The atomic weight of oxygen, based upon that of hydrogen, is 15.88, while the molecular weight, indicated by the specific gravity, is 31.76, showing oxygen to be diatomic, its molecular symbol being O_2. Generally, however, the atomic weight of oxygen is taken as 16.00 and is used as a standard upon which to base the atomic weights of the other elements, the atomic weight of hydrogen in such a system being 1.0075.

Atmospheric Oxygen. *It is possible to concentrate oxygen in air by mechanical means.* If air be slowly passed through a narrow tube of porous earthenware, surrounded by an outer jacket connected with an aspirator, the nitrogen, being slightly lighter than the oxygen, will diffuse through the porous wall into the outer jacket more rapidly than the oxygen, and the mixture passing out of the porous tube will be richer in oxygen than the air that entered it. The oxygen of the air dissolves in water in larger relative proportion than the nitrogen, so that air recovered from solution in water contains a larger proportion of oxygen than does ordinary air.

"Liquid Air." Air, which has a critical temperature of − 140° and a critical pressure of 39 atmospheres, may be liquefied, but so-called *liquid air* may contain as much as 54 per cent. of oxygen by weight, although air in gaseous condition contains only 23 per cent. of oxygen by weight. Moreover, when liquid air is evaporated, either spontaneously, or by boiling at − 190°, the nitrogen, which has a boiling point of − 194°, passes off first in almost pure condition, leaving the oxygen behind, until finally a liquid is obtained which contains as much as 94 per cent. by weight of oxygen.

Preparation of Oxygen. *For the preparation of oxygen we go ordinarily to the oxygen compounds — the oxides, hydroxides, and salts.*

Oxygen from Water. *Oxygen may be prepared from water, the most common of the oxides, by the dissociating action of heat.* We have already seen that when molten platinum is poured into water, the water is decomposed into a mixture of hydrogen and oxygen.

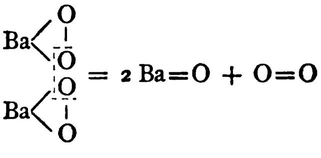
$$\begin{matrix}H-\vdots O\vdots-H\\H-\vdots O\vdots-H\end{matrix} = 2\,H-H + O=O$$

Oxygen from Oxides of Metals. *The oxides of some metals evolve all their oxygen when heated, forming a residue of the uncombined metal.* Mercuric oxide, HgO, a red powder, formed by carefully heating mercury in oxygen or air at low temperature, when strongly heated is readily decomposed into mercury and oxygen.

$$\begin{matrix}Hg=\vdots O\\Hg=\vdots O\end{matrix} = 2\,Hg + O=O$$

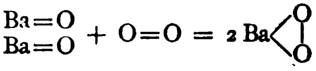
If a little mercuric oxide is heated in a glass tube, closed at one end, the mercury will be seen to sublime in bright globules on the walls of the tube, while the evolution of oxygen may be shown by the effect on a glowing splinter held at the mouth of the tube. To prepare larger quantities of oxygen, the mercuric oxide may be heated in a long glass tube placed in a furnace of Bunsen burners.

Peroxides. *Certain peroxides of metals, containing relatively high amounts of oxygen, evolve part of their oxygen when heated, forming residues of other lower, more stable, oxides of the elements.* Barium dioxide, BaO_2 (barium peroxide), a white or grayish white powder, when heated in a partial vacuum, gives up half of its oxygen, leaving a residue of barium monoxide, BaO.



$$2\,BaO_2 = 2\,Ba=O + O=O$$

By heating at lower temperature, in the presence of air forced into the retorts under pressure, the residue of barium monoxide, BaO, may be oxidized, forming barium dioxide, BaO_2.

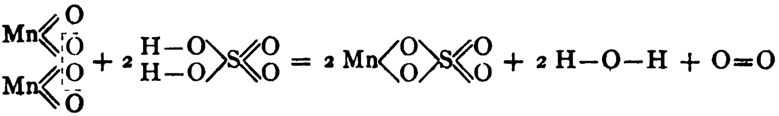


$$\begin{matrix}Ba=O\\Ba=O\end{matrix} + O=O = 2\,BaO_2$$

By again partially exhausting the retort, and increasing the temperature, the evolution of oxygen may be repeated, and the process may thus be made continuous without supplying more barium monoxide. This is *Brin's process* for the manufacture of oxygen.

Some peroxides may be acted upon by reagents with the evolution of oxygen, and the formation of salts containing a lower proportion of oxygen than was present in the peroxides.

Manganese dioxide, MnO_2 (manganese peroxide), may be acted upon by sulphuric acid, with the evolution of oxygen and the formation of manganous sulphate, $MnSO_4$.



Electrolysis of Hydroxides. *Certain hydroxides, which act as electrolytes, may be made to evolve oxygen, together with hydrogen, by the action of the electric current.* We have seen that the positive hydrogen-ions of sulphuric acid, in water solution and under the action of the current, are evolved as hydrogen, H_2, at the negative pole; and that the negative sulphur-oxygen-ions decompose at the positive pole, evolving oxygen, O_2, and forming sulphur trioxide, SO_3.

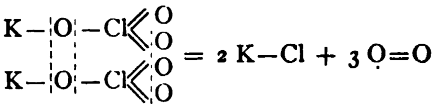
$$H_2SO_4 = 2\,\overset{+}{H} + \overset{-}{SO_4}$$
$$2\,\overset{+}{H} = H_2$$
$$2\,\overset{-}{SO_4} = 2\,SO_3 + O_2$$

Since the liberated sulphur trioxide combines with water to form more sulphuric acid, the process may be made a continuous one for the preparation of hydrogen and oxygen by the indirect decomposition of water by electricity. The hydrogen and oxygen may be evolved together and collected, as "detonating gas," or they may be collected separately.

We have seen likewise that some basic hydroxides, like sodium hydroxide, in solution and under the action of the electric current will evolve hydrogen and oxygen.

$$4\,\overset{+}{Na}\overset{-}{OH} = 4\,\overset{+}{Na} + 4\,\overset{-}{HO} = 4\,Na + 2\,H_2O + O_2$$
$$2\,Na + 2\,H_2O = 2\,NaOH + H_2$$

Oxygen from Salts. *Certain salts, containing oxygen, evolve oxygen when heated.* Potassium chlorate, $KClO_3$, rich in oxygen, readily decomposes when heated, continuing to evolve oxygen until a fused residue of potassium chloride is left behind.



The operation may be conducted to best advantage by mixing the potassium chlorate with an equal quantity of manganese dioxide, MnO_2, and gently heating the mixture in a round-bottomed flask or metal retort. The manganese dioxide helps the reaction by diffusing the heat throughout the mass, and thus preventing its fusion before the oxygen is all evolved, and it may also exert a "catalytic action," involving a temporary formation of potassium permanganate, $KMnO_4$, from which manganese dioxide is regenerated.

Oxygen may be evolved from some salts, rich in oxygen, by the action of suitable reagents. Potassium permanganate, $KMnO_4$, rich in oxygen, is readily decomposed by the action of sulphuric acid with the formation of potassium sulphate, K_2SO_4, manganous sulphate, $MnSO_4$, water, and oxygen.

$$2\,KMnO_4 + 6\,H_2SO_4 = 2\,K_2SO_4 + 4\,MnSO_4 + 6\,H_2O + 5\,O_2$$

Similarly, potassium dichromate, $K_2Cr_2O_7$, is readily acted upon by sulphuric acid, with formation of potassium sulphate, K_2SO_4, chromic sulphate, $Cr_2(SO_4)_3$, water, and oxygen.

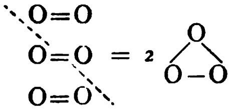
$$4\,K_2Cr_2O_7 + 8\,H_2SO_4 = 2\,K_2SO_4 + 2\,Cr_2(SO_4)_3 + 8\,H_2O + 3\,O_2$$

So also, the so-called bleaching powder, $CaOCl_2$, a compound resembling both calcium hypochlorite, $Ca(OCl)_2$, and calcium chloride, $CaCl_2$, gradually gives up its oxygen under the catalytic action of certain hydroxides, like cobaltous hydroxide, $Co(OH)_2$, or cobaltic hydroxide, $Co(OH)_3$.

$$CaOCl_2 + H_2O + 2\,Co(OH)_2 = CaCl_2 + 2\,Co(OH)_3$$

$$CaOCl_2 + 2\,Co(OH)_3 = 2\,Co(OH)_2 + CaCl_2 + H_2O + O_2$$

Ozone. *When oxygen is acted upon by a silent discharge of electricity, it acquires a peculiar odor and decreases in volume. Such oxygen may contain as much as 5 or 6 per cent. of an allotropic* *modification of oxygen, known as ozone, discovered by Schönbein in 1840.* When the oxygen containing ozone is heated, it increases in volume, and the ozone changes into ordinary oxygen. It has been found that the volume of the oxygen formed by heating ozone is 1½ times the volume of the ozone which is heated, from which we may conclude that the specific gravity, and therefore the molecular weight, of ozone is 48.00, or 1½ times the specific gravity and molecular weight of ordinary oxygen. While ordinary oxygen is diatomic, having the molecular symbol O_2, ozone appears to be triatomic, and may be represented by the molecular symbol O_3. We may represent the formation of ozone by the action of a silent discharge of electricity upon ordinary oxygen as a condensation of three molecules of oxygen into two molecules of ozone.



The formation of ordinary oxygen from ozone is the exact reverse of this reaction. A convenient form of apparatus for thus producing ozone is the *Siemens' tube*, which consists of two glass tubes, placed one within the other, and fitted with sheets of tin foil or other conducting substance, to which are attached the positive and negative terminals of an active induction coil. Through the annular space between the two tubes oxygen is passed in a slow stream, becoming converted into ozone during its passage.

Ozone is formed in small varying quantities in many of the reactions in which oxygen enters either as a product or as a factor. The liberation of oxygen from its oxides and other compounds is frequently accompanied by the formation of ozone. Small quantities of ozone are present in the oxygen liberated by the electrolysis of water containing dilute sulphuric acid, by the action of sulphuric acid upon manganese dioxide, and by the action of sulphuric acid upon potassium permanganate and upon potassium dichromate.

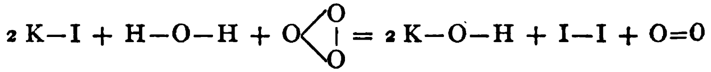
Slow Oxidation. *The slow oxidation of many substances is accompanied by the formation of ozone.* Air that has been for some time exposed to fuming yellow phosphorus, partly submerged in water in the bottom of a covered dish, contains ozone, as may be shown by exposing to its action strips of white paper, moistened with a solution of starch and potassium iodide, which, in the presence of ozone, will be rapidly colored blue.

$$6\,P + 9\,O_2 = 3\,P_2O_5 + O_3$$

Ozone is a gas, bluish in color when compressed, having a characteristic penetrating odor, and a harmful action when breathed in quantity. It is fifteen times more soluble in water than is ordinary oxygen. It may be condensed to an indigo-blue liquid at very low temperatures and high pressures, or even under ordinary atmospheric pressure at − 184°. It is probable that small quantities of ozone are present in fresh atmospheric air, though it is difficult to distinguish it from hydrogen dioxide, to which it is similar in many reactions.

The instability of ozone, and the consequent readiness with which it loses oxygen, makes it a very strong oxidizer. The liberated oxygen, momentarily in a dissociated condition, destroys many kinds of organic matter with great readiness, and even attacks some metals at ordinary temperature.

The slightest trace of ozone in a water solution of potassium iodide, KI, will form potassium hydroxide, KOH, and liberate iodine and oxygen. The potassium of the potassium iodide is oxidized to potassium oxide, which forms potassium hydroxide with the water.



$$2\,\text{K}-\text{I} + \text{H}-\text{O}-\text{H} + \text{O}<\begin{matrix}\text{O}\\ |\\ \text{O}\end{matrix} = 2\,\text{K}-\text{O}-\text{H} + \text{I}-\text{I} + \text{O}=\text{O}$$

If to the solution a little *starch emulsion*, made by pouring cold starch paste into a large quantity of boiling water and cooling, be added, the liberation of the least amount of iodine will be made evident by the formation of a bright blue *starch iodide* on the paper. In case the absence of other oxidizing agents which would effect the same result can be established, the blue coloration of the starch test-paper may indicate the presence of ozone.

Hydrogen Monoxide, or Water. *Of the oxygen compounds, hydrogen monoxide, or water, is the most common.* We have already noted that *hydrogen monoxide* or *water* may be formed by the direct combination of hydrogen with oxygen,

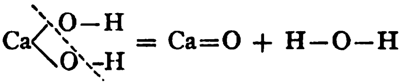
$$2\,\text{H}-\text{H} + \text{O}=\text{O} = 2\,\text{H}-\text{O}-\text{H}$$

and have observed in detail its physical and chemical properties. We may recall that the hydrogen burns quietly in an open vessel exposed to a free surface of oxygen, but explosively when mixtures of hydrogen and oxygen are ignited. A cold surface introduced into a hydrogen flame will be covered with water formed by the burning hydrogen.

Water under normal atmospheric pressure freezes ordinarily at 0°, and boils at 100°, although both freezing point and boiling point are altered by changes in pressure and by the presence of substances dissolved in the water. The critical temperature of water is 370° and its critical pressure is 195.5 atmospheres. *Liquid water*, ordinarily colorless, appears greenish blue when viewed through a thick layer, and is tasteless when pure. Its volume is slightly affected by pressure changes, but noticeably so by changes in temperature, since it occupies its least bulk, under 760 mm. pressure, latitude 45°, at 4°. One cubic centimeter of water at 4°, 760 mm. pressure, latitude 45°, weighs 1 gram, and water in this condition has a specific gravity of 1. The specific heat of water is 1 common calorie, its latent heat of fusion is 79 common calories, and its latent heat of vaporization is 536 common calories. *Ice*, the solid phase of water, is a transparent solid, having a bluish or greenish tinge when viewed in large clear masses, but appearing a brilliant white when in finely divided particles which reflect the light irregularly. Ice forms hexagonal crystals, best observed in snowflakes. The specific gravity of ice is 0.9173. *Steam* is a colorless vapor, of specific gravity 18.02.

Water in the World. *Water is of great importance in the world.* The ocean water is evaporated, raised to the higher regions by air currents, blown about in partially condensed clouds by the wind, precipitated as rain or snow, and finally carried in rivers back into the ocean. Large bodies of water equalize the climate by absorbing and giving out heat, while the erosive effect of waves and currents and the disintegrating action of the frost have given shape to the continents, at the same time forming fertile soils and sedimentary rocks. By the solvent action of water upon solid substances, the plant food in the ground is made available for absorption and assimilation into the bodies of plants, and water similarly assists in the digestion and assimilation of food by animals. All plants and animal bodies contain a large proportion of water.

Water in Chemical Changes. *Water is a factor or a product in a great many chemical changes, and by its solvent action it influences many reactions in which its own composition is not affected.* In many cases water may be set free from compounds which contain hydrogen and oxygen. Thus, many hydroxides, like calcium hydroxide, evolve water when they are heated.



Water is formed when many substances containing hydrogen are oxidized, as when hydrogen sulphide, H_2S, is burned in air or oxygen,

$$2\,H_2S + 3\,O_2 = 2\,SO_2 + 2\,H_2O$$

when methane, CH_4, and other similar hydrocarbons, are burned in air or oxygen,

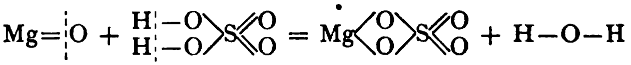
$$CH_4 + 2\,O_2 = 2\,H_2O + CO_2$$

and when alcohols, ethers, organic acids, carbohydrates, and proteids, are completely oxidized.

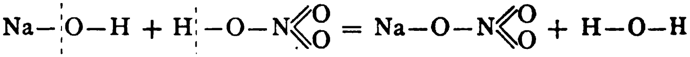
Water may be formed by reducing some oxides, such as cupric oxide, CuO, with hydrogen.

$$CuO + H_2 = Cu + H_2O$$

The action of acids upon basic oxides and basic hydroxides is accompanied by the formation of water. Thus, we have water formed when magnesium oxide, MgO, is acted upon by sulphuric acid,



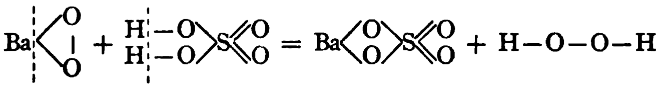
and when sodium hydroxide and nitric acid neutralize one another.



It has been shown that many substances when in solution in water take part in chemical changes which might not otherwise be possible. Water sometimes brings about the oxidation of substances by its own decomposition. It is acted upon by chlorine and bromine, forming hydrogen chloride and hydrogen bromide respectively, and liberating oxygen, which at the moment of its formation is especially active. At high temperatures water will oxidize carbon, setting free hydrogen. Water is an oxide of great stability, being composed of the strongly electro-positive hydrogen combined with the strongly electro-negative oxygen, and yields only to the most powerful means of decomposition.

The dissociation of pure water by heat begins at 1000°, and progresses with increase of temperature, while pure water, a non-conductor of electricity, is not appreciably decomposed by the electric current.

Hydrogen Dioxide. *A second compound of hydrogen and oxygen, hydrogen dioxide, richer in oxygen than hydrogen monoxide, may be made by acting upon certain peroxides with acids.* When barium dioxide, BaO_2, mixed with a small quantity of water, is gradually added to cold dilute sulphuric acid, white barium sulphate, $BaSO_4$, is precipitated and may be removed by filtering, while *hydrogen dioxide*, H_2O_2 (hydrogen peroxide), will remain in solution.



Instead of sulphuric acid, hydrochloric acid or even carbonic acid may be employed. By evaporating the water solution of hydrogen dioxide at 70° on a water bath, a 45 per cent. solution may be obtained, and by evaporating it under reduced pressure it may be obtained in nearly anhydrous condition.

Small quantities of hydrogen dioxide are also formed by the direct combination of oxygen with hydrogen, and with water. When oxygen or air is passed through water, containing sulphuric acid undergoing electrolysis, hydrogen dioxide is found in the solution at the negative pole where the hydrogen is set free.

$$H-H + O=O = H-O-O-H$$

When oxygen or air is shaken with finely divided zinc and dilute sulphuric acid, hydrogen dioxide is formed by the combination of the hydrogen, liberated from the sulphuric acid, with the oxygen of the air.

$$Zn + H_2SO_4 + O_2 = ZnSO_4 + H_2O_2$$

Appreciable quantities of hydrogen dioxide may be formed by a similar combination of hydrogen and oxygen when air is shaken with finely divided zinc and water.

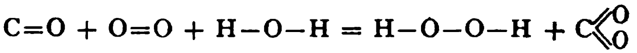
$$Zn + 2\,H_2O + O_2 = Zn(OH)_2 + H_2O_2$$

When yellow phosphorus, partly covered by water, is allowed to slowly oxidize, the air above the phosphorus is found to contain ozone, and the water is found to contain hydrogen dioxide, formed by the combination of some of the active dissociated oxygen, set free by the phosphorus, with the water.

$$2\,P + 3\,O_2 + H_2O = P_2O_5 + H_2O_2$$

A similar formation of hydrogen dioxide and ozone takes place when a flame of burning hydrogen or carbon monoxide is cooled suddenly, by allowing it to impinge upon a surface of water.

$$\mathrm{H-H + O{=}O = H-O-O-H}$$

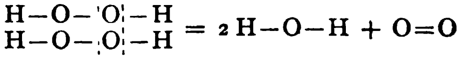


$$\mathrm{C{=}O + O{=}O + H-O-H = H-O-O-H + C{\begin{smallmatrix}\diagup O\\ \diagdown O\end{smallmatrix}}}$$

Hydrogen dioxide, H_2O_2 (hydrogen peroxide), is a sirupy liquid, of specific gravity 1.49, ordinarily colorless, but bluish when viewed in a thick layer. It is very soluble in water, and its solutions have an astringent, bitter taste. It evaporates when exposed to air and when heated. It is used as an antiseptic in medicine and in bleaching coloring matters.

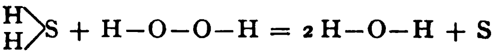
Reduction of Hydrogen Dioxide.

Hydrogen dioxide, like ozone, is very unstable, evolving oxygen in dissociated condition, and is therefore a strong oxidizer. Hydrogen dioxide in concentrated solution is constantly giving off some of its oxygen, and sometimes explodes violently. It is completely decomposed, when heated, into water and oxygen.



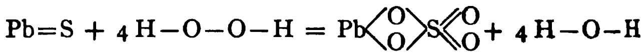
$$\begin{matrix}\mathrm{H-O-O\vdots-H}\\ \mathrm{H-O-O\vdots-H}\end{matrix} = \mathrm{2\,H-O-H + O{=}O}$$

Hydrogen dioxide will remove the hydrogen from hydrogen sulphide, H_2S, forming water, and depositing sulphur,



$$\mathrm{{\begin{smallmatrix}H\diagdown\\ H\diagup\end{smallmatrix}}S + H-O-O-H = 2\,H-O-H + S}$$

while lead sulphide, PbS, is oxidized by it to lead sulphate, $PbSO_4$.

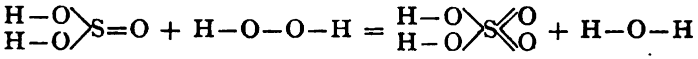


$$\mathrm{Pb{=}S + 4\,H-O-O-H = Pb{\begin{smallmatrix}\diagup O\diagdown\\ \diagdown O\diagup\end{smallmatrix}}S{\begin{smallmatrix}\diagup O\\ \diagdown O\end{smallmatrix}} + 4\,H-O-H}$$

Advantage may be taken of this action to brighten up old oil paintings which have become discolored by long exposure of the lead compounds of the paint to air containing traces of hydrogen sulphide.

The sulphides of other metals are similarly oxidized by hydrogen dioxide.

Many compounds containing oxygen may be oxidized by hydrogen dioxide. Sulphurous acid, H_2SO_3, is changed by it into sulphuric acid,



and chromic acid, H_2CrO_4, is changed by it into unstable perchromic acid, $H_2Cr_2O_8$, which gives a characteristic blue color to ether.

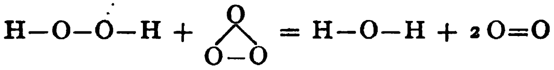
$$2\,H_2CrO_4 + H_2O_2 = H_2Cr_2O_8 + 2\,H_2O$$

Hydrogen dioxide, like ozone, liberates iodine from potassium iodide, KI, potassium hydroxide being formed in solution.

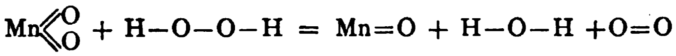
$$2\,K-I + H-O-O-H = 2\,K-O-H + I-I$$

The presence of the free iodine in the solution may be indicated by its action in giving a blue coloration to paper moistened with a solution of potassium iodide and starch.

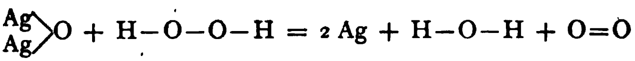
Sometimes hydrogen dioxide acts indirectly as a reducer. When hydrogen dioxide acts upon ozone, water and ordinary oxygen are formed.



The dissociated oxygen liberated from the hydrogen dioxide reduces the ozone. By a similar action certain higher oxides are reduced to lower oxides, and some oxides are completely reduced to metals by hydrogen dioxide. Manganese dioxide, MnO_2, is reduced by hydrogen dioxide, H_2O_2, to manganous oxide, MnO,



and silver oxide, Ag_2O, is in like manner reduced to silver.



The *oxides* of elements other than hydrogen, as well as the *hydroxides*, both bases and acids, and the *salts* which contain oxygen, are best studied in detail in connection with the elements which characterize them individually.

Oxidation and Combustion. Oxygen is the most electro-negative of all the elements, standing below all other elements in the electro-chemical series. It has a strong attraction for most of the other elements. It will combine with all the elements except bromine, fluorine, and the inert atmospheric elements, to form oxides. Some elements, like sodium and potassium, at ordinary temperature oxidize spontaneously, becoming covered with a thin film of oxide, while at a higher temperature they oxidize with great rapidity, evolving a great deal of heat, and forming a *flame* of gaseous products in a state of incandescence. Such rapid oxidation is known as *combustion* or *burning*, and the temperature at which it takes place spontaneously is known as the *kindling temperature* or *point of ignition*. Phosphorus, which oxidizes slowly at ordinary temperatures without flame, is readily ignited, when it burns with great violence; while sulphur may be oxidized only by heating it to its point of ignition. Aluminium, copper, iron, and other similar metals do not combine with oxygen spontaneously at ordinary temperatures, and most metals can be made tó burn with a flame only when heated exceedingly hot. A piece of iron wire, however, will burn with violence when ignited in an atmosphere of oxygen.

Many compounds will interact with oxygen, with the formation of oxides of their characteristic elements, and some compounds, such as the hydrocarbons and carbohydrates, are inflammable, and are used as fuels. Both elements and compounds may be oxidized indirectly, by heating them with oxides or with other oxygen compounds, which will give up their oxygen. Processes of combustion in pure oxygen, as well as the many processes of slow oxidation of substances exposed to the atmosphere, are aided by the presence of water. Some substances, like carbon and phosphorus, combustible in moist oxygen under certain conditions of temperature, may, in a perfectly dry state, be exposed to dry oxygen at the same or even higher temperatures without becoming oxidized. Water sometimes acts as an agent of indirect oxidation, being acted upon by some substances with the liberation of oxygen, which in the moment of formation is especially active. Thus, while dry chlorine will not act upon organic dyes in dry condition, such coloring matters are readily bleached by chlorine in the presence of moisture. When some kinds of damp organic matter are confined tightly, they may absorb oxygen sufficiently to raise their temperature to the ignition point, resulting in *spontaneous combustion*. Cotton or woolen rags, mixed with oil or other matter capable of absorbing oxygen, frequently take fire spontaneously.

Oxidation plays an important part in animal and vegetable physiology. Both plants and animals by the process of *respiration* cause the oxidation of food and tissue with the liberation of heat and mechanical energy. On the other hand, plants are able, in the process of *photosynthesis*, or formation of organic compounds under the influence of sunlight, to liberate oxygen from carbon dioxide, while assimilating the carbon.

Sulphur, S, 32.06

Sulphur Minerals. Sulphur, a solid, usually bright yellow in color, is found in volcanic regions, notably in Sicily, in free condition, rarely in beautifully crystallized rhombic octahedra, and more generally in intermixture with gypsum, or calcite, or other minerals. It is also found in combination in the widely distributed sulphides and sulphates. The principal mineral sulphides are *pyrite*, FeS_2; *cinnabar*, HgS; *sphalerite*, ZnS; *stibnite*, Sb_2S_3; *realgar*, As_2S_2; and *orpiment*, As_2S_3. The most important natural sulphates are *gypsum*, $CaSO_4 \cdot 2\,H_2O$; *anhydrite*, $CaSO_4$; *barite*, $BaSO_4$; *kieserite*, $MgSO_4 \cdot H_2O$. Although some sulphur is obtained commercially from natural sulphides which are worked for their metallic constituents, and from the sulphide residues of the Leblanc soda process and of the illuminating gas manufacture, the greater part of the sulphur of commerce comes from the natural deposits of the free element in Sicily.

Preparation. In this region, where ordinary fuel is scarce, the extremely wasteful method of burning up a part of the sulphur to secure the heat necessary to melt the remainder out of the crude ore is still in use. The ore is so stacked in pits as to leave vertical air flues, and is kindled at the bottom. After the mass of air is sufficiently heated, by the burning of one fourth or one third of the sulphur, the kiln is closed, and the remaining sulphur melts and drains to the bottom. The crude sulphur is further purified by distillation from cast-iron retorts, the sulphur vapor being condensed rapidly in cooled stone chambers to the yellow crystalline powder known as *flowers of sulphur*, and less rapidly to molten sulphur which is run into molds to make roll sulphur.

Allotropic Forms. When roll sulphur is slowly heated, it melts at 115°–120° to a mobile amber-colored liquid, which darkens as the temperature rises, becomes so viscid at 250° that it will no longer flow, at a still higher temperature is again mobile, and boils at 448°, with formation, under ordinary pressure, of an orange-yellow vapor.

Ordinary roll sulphur dissolves in carbon disulphide, and from such a solution, when allowed to evaporate spontaneously, the sulphur separates as *octahedral sulphur* in crystals of the orthorhombic system, similar to the native crystals, of specific gravity 2.07, hard, brittle, electrified negatively by friction, insoluble in water, slightly soluble in alcohol and in ether, and easily dissolved by carbon disulphide, melting at 114.5°.

When a solution of sulphur in carbon disulphide is heated in a sealed tube to 100°, and then cooled, *prismatic sulphur* separates at first in transparent monoclinic crystals, very pale in color, behaving toward solvents like the octahedral sulphur, but having the lower specific gravity 1.96, and the melting point 120°. On standing, though still keeping their outer prismatic form, the monoclinic crystals give evidences of instability, becoming opaque aggregations of minute octahedral crystals, of specific gravity 2.07.

When melted sulphur cools slowly, it generally solidifies as the unstable variety, crystallizing in long monoclinic prisms which may best be seen by breaking the top crust before solidification is complete, and pouring out the still liquid sulphur. These monoclinic crystals, however, soon disintegrate to minute orthorhombic crystals, and when the melted sulphur happens to be supercooled to 90° without solidifying, it crystallizes at once to the octahedral variety. Roll sulphur, when freshly made, consists chiefly of a mass of monoclinic prisms, but gradually goes over into the orthorhombic forms, taking the higher specific gravity.

Besides these two solid crystalline varieties, another solid modification of sulphur may be obtained by heating sulphur to about 230° and pouring the resulting liquid, while hot enough to be viscous, into cold water. The *plastic amorphous sulphur* thus formed is a yellowish brown, soft solid, of specific gravity 1.92, less than that of either of the crystalline varieties, and is partly soluble in carbon disulphide. At ordinary temperatures plastic sulphur passes slowly into the rhombic variety, and at 95° the conversion is immediate.

The *flowers of sulphur* formed by the sudden cooling of sulphur vapor apparently contains, besides the rhombic sulphur which can be dissolved out by carbon disulphide, still another variety of sulphur which is white, amorphous, and insoluble in carbon disulphide.

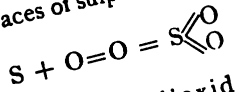
The white amorphous *milk of sulphur* used in medicine and obtained by adding an acid to a solution of a polysulphide, and the *colloidal sulphur*, formed by the action of sulphur monochloride upon water, or of hydrogen sulphide upon hydrogen dioxide, appear to consist of rhombic sulphur so finely divided as to be very sensitive chemically, and prone to remain in liquid suspension or pseudo-solution.

The occurrence of these varieties of sulphur, the rhombic, prismatic, plastic, insoluble amorphous, finely divided, and colloidal solid forms, as well as the mobile and the viscid forms of molten sulphur, suggests the he oxides, sulphur dioxide, SO_2, and sulphur trioxide, SO_3, are made by oxidizing sulphur, while the other two oxides are rare. e hydroxides, the oxygen acids, H_2SO_4, H_4SO_5, $H_2S_2O_7$, known at ble temperatures as crystalline substances, and H_6SO_6, a liquid, may nade by combining sulphur trioxide, SO_3, with appropriate amounts water. The solution of sulphur dioxide, SO_2, in water acts like an d, and it may be considered to be a solution of unstable sulphurous id, H_2SO_3. The other hydroxides, the thio-acids, are more or less nstable, and are known only in solution.

Sulphur Oxides. *We shall study first the sulphur oxides, and of these sulphur dioxide and sulphur trioxide are most important.*

Sulphur Dioxide. *Sulphur dioxide may be made by burning sulphur in oxygen or air, or by heating sulphur in contact with some easily reducible oxide, or by similarly oxidizing a sulphide.*

When a piece of sulphur is ignited in oxygen or air, it burns quietly with a characteristic pale blue flame, forming *sulphur dioxide*, SO_2, a colorless gas, mixed with traces of sulphur trioxide formed simultaneously.



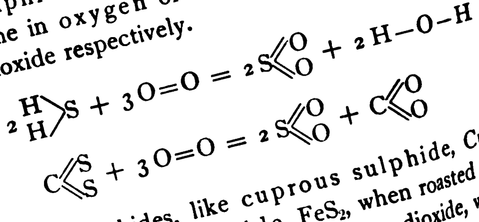
$$\mathrm{S} + \mathrm{O{=}O} = \mathrm{S}\begin{array}{l}=\mathrm{O}\\ =\mathrm{O}\end{array}$$

Cupric oxide, CuO, manganese dioxide, MnO_2, and many other oxides may serve as oxidizers of sulphur.

$$2\,\mathrm{S} + 2\,\mathrm{CuO} = \mathrm{SO_2} + \mathrm{Cu_2S}$$

$$2\,\mathrm{S} + \mathrm{MnO_2} = \mathrm{SO_2} + \mathrm{MnS}$$

Many sulphides are likewise easily oxidized. Thus, the gaseous hydrogen sulphide, H_2S, and the liquid carbon disulphide, CS_2, burn with flame in oxygen or air, forming sulphur dioxide and water and carbon dioxide respectively.



$$2\,\begin{array}{r}\mathrm{H}\diagdown\\ \mathrm{H}\diagup\end{array}\!\mathrm{S} + 3\,\mathrm{O{=}O} = 2\,\mathrm{S}\begin{array}{l}=\mathrm{O}\\ =\mathrm{O}\end{array} + 2\,\mathrm{H{-}O{-}H}$$

$$\mathrm{C}\begin{array}{l}=\mathrm{S}\\ =\mathrm{S}\end{array} + 3\,\mathrm{O{=}O} = 2\,\mathrm{S}\begin{array}{l}=\mathrm{O}\\ =\mathrm{O}\end{array} + \mathrm{C}\begin{array}{l}=\mathrm{O}\\ =\mathrm{O}\end{array}$$

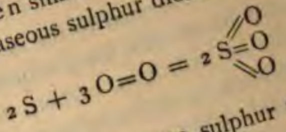
Certain solid sulphides, like cuprous sulphide, Cu_2S, zinc sulphide, ZnS, and iron disulphide, FeS_2, when roasted in air, leave an oxide, while the sulphur is oxidized to sulphur dioxide, which is on th

up entirely on boiling. Sulphur dioxide is therefore the anhydride
he unstable sulphurous acid.

$$SO_2 + H_2O = H_2SO_3$$

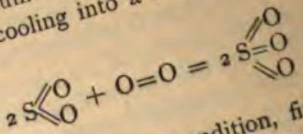
Sulphur Trioxide.

Sulphur trioxide may be formed in small amounts by th
direct oxidation of sulphur in oxygen or air. When su
phur is burned in oxygen small quantities of *sulphur trioxide*, SO_3, a
formed along with the gaseous sulphur dioxide, as a white mist.



$$2\,S + 3\,O{=}O = 2\,S(=O)_3$$

It is not possible, however, to prepare sulphur trioxide in quantity
simply burning sulphur.
Sulphur trioxide may be easily formed in quantity by the direct oxi
tion of sulphur dioxide by heating in oxygen or air, in the presence of c
tain catalytic substances. When a dry mixture of sulphur dioxid
SO_2, and oxygen or air is passed over gently heated, finely divid
platinum, dense white fumes of *sulphur trioxide*, SO_3, are formed whi
may be condensed by cooling into a colorless liquid or white need
shaped crystals.



$$2\,S(=O)_2 + O{=}O = 2\,S(=O)_3$$

Instead of the platinum in pure condition, finely divided asbes
coated with a deposit of platinum, may be employed.
Certain oxides may be similarly employed to oxidize sulphur diox
Thus when sulphur dioxide is brought in contact with chromi
trioxide, CrO_3, sulphur trioxide and chromic oxide, Cr_2O_3, are form

$$6\,SO_2 + 4\,CrO_3 = 6\,SO_3 + 2\,Cr_2O_3$$

Manganese dioxide, MnO_2, ferric oxide, Fe_2O_3, and other oxides
cause the oxidation of sulphur dioxide to sulphur trioxide.
Sulphur trioxide may also be formed by the decomposition of c
compounds which contain its constituent elements, such as sul
acid and disulphuric acid, and some salts of these acids.
trioxide may be made in the laboratory, and is sometimes manu
commercially by heating sodium disulphate alone or with sulph
or by heating ferrous sulphate or ferric sulphate.

disulphur trioxide and water are brought into direct contact, the
on is violent, sulphur, sulphur dioxide, sulphuric acid, and other
plex thio-acids, which we shall study later, being formed. Disulphur
ide does, however, act without violence upon disulphuric acid,
$_2O_7$, a hydroxide in which the water of constitution is held firmly,
l it may be that by this action the known but unstable *hyposulphurous*
id, $H_2S_2O_4$, of which disulphur trioxide may be the anhydride, is
rmed, although it is broken up in the direct action of disulphur
rioxide upon water.

Sulphur Heptoxide.

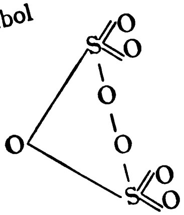
Sulphur heptoxide, S_2O_7, the highest oxide of sulphur, may be obtained by the action of a silent electrical discharge of high intensity upon a mixture of sulphur dioxide and oxygen.

$$4\,SO_2 + 3\,O_2 = 2\,S_2O_7$$

In this manner oily drops are formed which crystallize at 0°, are unstable at ordinary temperature, and immediately decompose on heating into sulphur trioxide and oxygen.

$$2\,S_2O_7 = 4\,SO_3 + O_2$$

When sulphur heptoxide is added to water, a violent action ensues, with evolution of heat and the formation of sulphuric acid and free oxygen. If, however, sulphur heptoxide is added to a water solution of sulphuric acid, the action is less violent, the temperature is lower, and in the solution there is formed, besides sulphuric acid, an acid having the composition $H_2S_2O_8$, known as *persulphuric acid*. Taking into consideration the properties of persulphuric acid, of which sulphur heptoxide may be regarded as the anhydride, the constitution of sulphur heptoxide may be best represented by the symbol



Sulphurous Acid.

A solution of the unstable sulphurous acid may be made most easily by passing a stream of gaseous sulphur dioxide into water to saturation. Such a solution gives off sulphur dioxide, SO_2, slowly when exposed to the air, and rapidly and entirely on boiling. At 0° colorless cubical crystals separate, which appear to have the composition $H_2SO_3 \cdot 6\,H_2O$. Although sulphurous acid is itself unstable nitrogen tetroxide, N_2O_4, sulphuric acid and nitrogen dioxide, NO, are formed.

$$H_2SO_3 + N_2O_3 = H_2SO_4 + 2\,NO$$
$$2\,H_2SO_3 + N_2O_4 = 2\,H_2SO_4 + 2\,NO$$

Since nitrogen dioxide will combine spontaneously with the oxygen of the air to form nitrogen trioxide and nitrogen tetroxide, these nitrogen oxides may be employed in the continuous formation of sulphuric acid from sulphurous acid.

When sulphurous acid acts upon lead dioxide, PbO_2, a white precipitate of lead sulphate, $PbSO_4$, is formed. We may write the reaction as consisting first in the formation of lead monoxide, PbO, which is subsequently acted upon by sulphuric acid.

$$H_2SO_3 + PbO_2 = H_2SO_4 + PbO$$
$$PbO + H_2SO_4 = PbSO_4 + H_2O$$

Sulphurous acid will reduce certain higher acidic hydroxides with the formation of sulphuric acid. Sulphurous acid reduces nitric acid, forming nitrogen dioxide, NO, or various other products according to the conditions.

$$3\,H_2SO_3 + 2\,HNO_3 = 3\,H_2SO_4 + H_2O + 2\,NO$$

When sulphurous acid is added to the red solution of chromic acid, H_2CrO_4, the liquid turns green on account of the formation of chromic sulphate, $Cr_2(SO_4)_3$. We may consider the reaction to consist first in the formation of chromic oxide, Cr_2O_3, which is then acted upon by sulphuric acid.

$$3\,H_2SO_3 + 2\,H_2CrO_4 = 3\,H_2SO_4 + 2\,H_2O + Cr_2O_3$$
$$Cr_2O_3 + 3\,H_2SO_4 = Cr_2(SO_4)_3 + 3\,H_2O$$

Other acidic hydroxides, such as chloric acid, $HClO_3$, bromic acid, $HBrO_3$, and iodic acid, HIO_3, yield their oxygen to sulphurous acid.

Sulphurous acid may be oxidized by certain salts rich in oxygen. The purple solution of potassium permanganate, $KMnO_4$, is bleached by sulphurous acid, with the formation of sulphuric acid and other products.

$$5\,H_2SO_3 + 2\,KMnO_4 = 2\,MnSO_4 + K_2SO_4 + 2\,H_2SO_4 + 3\,H_2O$$

Sulphurous acid may be oxidized indirectly by the oxygen separated from water in the simultaneous action of sulphurous acid and certain

Uses of Sulphurous Acid. The strong chemical activity of sulphurous acid renders it of much importance. It is largely employed as a reducer in the laboratory and in manufacturing operations. It is detrimental to the growth of molds and other small organisms, and is used in breweries and elsewhere as an antiseptic. If present in sufficient quantities, it will destroy the life of the larger plants, as may be seen by its effect on vegetation in neighborhoods where large amounts of sulphur or of fuels containing sulphur are burned.

Bleaching. Sulphurous acid acts readily upon many organic coloring matters, such as are found in the leaves of flowers, and in silk, wool, and straw tissues, forming compounds which are colorless. It is, therefore, largely used for *bleaching* or decolorizing such substances as would be injured by chlorine or other more powerful agents. The materials to be bleached are suspended in moist condition, in a closed space, in which the fumes from burning sulphur are allowed to pass, and are finally washed thoroughly to remove the sulphur compounds. The bleaching action of sulphurous acid is not permanent, however, since the compounds formed with the coloring matter gradually break down spontaneously, or immediately when acted upon by acids or bases, permitting a color either like or unlike the original to return in the tissue. A bunch of bright-colored flowers moistened and placed in a closed vessel containing sulphur dioxide will turn white, but when allowed to stand in air they may gradually become colored again. Sulphurous acid is sometimes used as an "antichlor" to remove the excess of chlorine from cotton or woolen fabrics that have been bleached with this substance.

Sulphites. *By the interaction of sulphurous acid with bases, or with carbonates of positive elements, we may obtain neutral and acidic sulphites in which sulphur is in the negative ion.* Sodium hydroxide gives with sulphurous acid, H_2SO_3, the neutral *sodium sulphite*, Na_2SO_3, or the acidic *sodium hydrogen sulphite*, $NaHSO_3$, according to the proportions of the reacting substances.

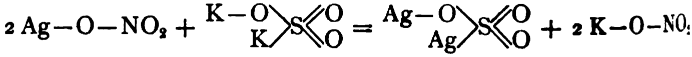
$$2\,Na\mathrm{OH} + H_2\mathrm{SO_3} = Na_2\mathrm{SO_3} + 2\,\mathrm{H_2O}$$
$$Na\mathrm{OH} + H\mathrm{HSO_3} = Na\mathrm{HSO_3} + \mathrm{H_2O}$$

The same compounds may be made by acting upon sodium carbonate with sulphurous acid in proper proportions.

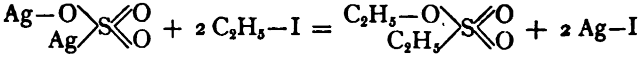
$$Na_2\mathrm{CO_3} + H_2\mathrm{SO_3} = Na_2\mathrm{SO_3} + \mathrm{CO_2} + \mathrm{H_2O}$$
$$Na_2\mathrm{CO_3} + 2\,H\mathrm{HSO_3} = 2\,Na\mathrm{HSO_3} + \mathrm{CO_2} + \mathrm{H_2O}$$

Sulphurous acid does not, however, act upon most metals.

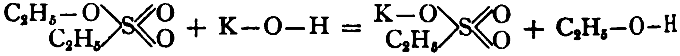
On the other hand, when silver sulphite, Ag_2SO_3, precipitated by the action of potassium sulphite, K_2SO_3, upon silver nitrate, $AgNO_3$, is made to act upon ethyl iodide, C_2H_5I, a second compound of the composition $(C_2H_5)_2SO_3$, boiling at 213.4°, is formed. By the action of potassium hydroxide upon the second ethyl compound, only one of the ethyl groups is replaced by potassium, ethyl alcohol, C_2H_5OH, and the compound $K(C_2H_5)SO_3$ resulting, from which by the action of phosphorus pentachloride, PCl_5, the potassium and some oxygen may be replaced by chlorine, giving the compound $Cl(C_2H_5)SO_2$. This chlorine compound in turn may be reduced by hydrogen, thereby losing its chlorine and oxygen, yielding ethyl hydrogen sulphide, C_2H_5SH. Since in ethyl hydrogen sulphide we know that the one remaining ethyl group is combined directly to the sulphur, we may conclude that it was so directly combined in the compounds $Cl(C_2H_5)SO_2$, $K(C_2H_5)SO_3$, and $(C_2H_5)_2SO_3$ from which the ethyl hydrogen sulphide was derived by substitution. Accordingly it may be supposed that in silver sulphite, Ag_2SO_3, one of the silver atoms is combined to the sulphur directly, and that in the potassium sulphite, K_2SO_3, from which the silver sulphite is made, one of the potassium atoms is similarly directly combined.

(1) 

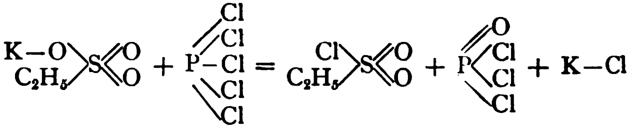
$$2\,Ag{-}O{-}NO_2 + \begin{matrix}K{-}O\\K\end{matrix}{>}S{<}\begin{matrix}O\\O\end{matrix} = \begin{matrix}Ag{-}O\\Ag\end{matrix}{>}S{<}\begin{matrix}O\\O\end{matrix} + 2\,K{-}O{-}NO_2$$

(2) 

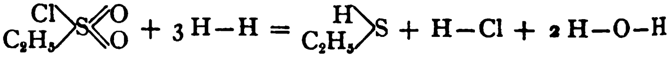
$$\begin{matrix}Ag{-}O\\Ag\end{matrix}{>}S{<}\begin{matrix}O\\O\end{matrix} + 2\,C_2H_5{-}I = \begin{matrix}C_2H_5{-}O\\C_2H_5\end{matrix}{>}S{<}\begin{matrix}O\\O\end{matrix} + 2\,Ag{-}I$$

(3) 

$$\begin{matrix}C_2H_5{-}O\\C_2H_5\end{matrix}{>}S{<}\begin{matrix}O\\O\end{matrix} + K{-}O{-}H = \begin{matrix}K{-}O\\C_2H_5\end{matrix}{>}S{<}\begin{matrix}O\\O\end{matrix} + C_2H_5{-}O{-}H$$

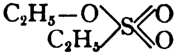
(4) 

$$\begin{matrix}K{-}O\\C_2H_5\end{matrix}{>}S{<}\begin{matrix}O\\O\end{matrix} + \begin{matrix}&Cl\\&Cl\\P&{-}Cl\\&Cl\\&Cl\end{matrix} = \begin{matrix}Cl\\C_2H_5\end{matrix}{>}S{<}\begin{matrix}O\\O\end{matrix} + \begin{matrix}&O\\&Cl\\P&\\&Cl\\&Cl\end{matrix} + K{-}Cl$$

(5) 

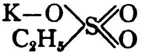
$$\begin{matrix}Cl\\C_2H_5\end{matrix}{>}S{<}\begin{matrix}O\\O\end{matrix} + 3\,H{-}H = \begin{matrix}H\\C_2H_5\end{matrix}{>}S + H{-}Cl + 2\,H{-}O{-}H$$

These reactions would seem to indicate that the second of the two ethyl compounds of the composition $(C_2H_5)_2SO_3$ is an ***unsymmetrical ethyl sulphite***, or ***ethyl sulphonate***,



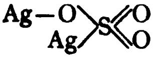
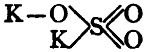
$$\begin{matrix}C_2H_5{-}O\\C_2H_5\end{matrix}{>}S{<}\begin{matrix}O\\O\end{matrix}$$

and that the compound $K(C_2H_5)SO_3$ is an ***unsymmetrical potassium ethyl sulphite***, or ***potassium ethyl sulphonate***,



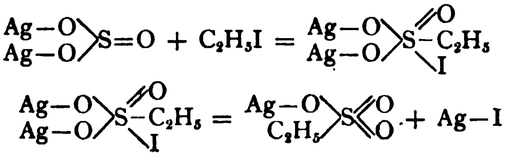
$$\begin{matrix}K{-}O\\C_2H_5\end{matrix}{>}S{<}\begin{matrix}O\\O\end{matrix}$$

and furthermore that both silver sulphite and potassium sulphite may in part at least have the unsymmetrical constitution of the so-called sulphonates, as represented by the symbols

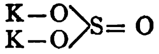

and


respectively.

It cannot be said with certainty, however, that the existence of sulphonates or unsymmetrical sulphites containing carbon radicals is a proof that the silver salt of the composition Ag_2SO_3 is unsymmetrical, nor is the proof positive that the more electro-positive elements such as potassium and sodium are able to form unsymmetrical sulphites. Thus, ethyl iodide, C_2H_5I, will act upon certain compounds of polyvalent elements to form unstable addition products, which may decompose to form other compounds of the elements different in constitution from the compounds originally acted upon. It is quite possible to suppose that ethyl iodide might form with symmetrical silver sulphite, Ag_2SO_3, an addition product such as $Ag_2SO_3 \cdot C_2H_5I$, which might decompose into unsymmetrical silver ethyl sulphite, $Ag(C_2H_5)SO_3$ and silver iodide.



If this be true, then an unsymmetrical sulphite of a carbon radical might be derived from a symmetrical metal sulphite as well as from a sulphite of unsymmetrical constitution. In the absence of proof of other structure it will be simpler in our discussion of the sulphites to assume the symmetrical structure, such as



for the metal sulphites, though it is a possibility, and if we take into consideration certain relations brought out by the study of certain sulphites containing more than one positive element, it is even probable, that unsymmetrical sulphites of common elements, similar to the sulphonates of carbon radicals, may actually exist.

Sodium Sulphite. Both sodium sulphites are white and are soluble in water. The normal *sodium sulphite*, Na_2SO_3, may be obtained as large crystals, having the composition $Na_2SO_3 \cdot 7\,H_2O$, which become anhydrous at 150°. It is used in photography in "developer" solutions, in which it serves to preserve the active inorganic compounds from the action of the air. The *sodium hydrogen sulphite*, $NaHSO_3$, is a very deliquescent white powder, which upon standing may evolve water and sulphur dioxide, becoming changed into the normal sodium sulphite. Both compounds are used as antiseptics and in bleaching and dyeing. The potassium salts of sulphurous acid, like the sodium salts, are white and soluble.

Oxidation of Sulphites. *The soluble sulphites, like sulphurous acid, are strong reducers, uniting with oxygen free as well as combined, becoming thereby changed into sulphates.* Thus, when sodium sulphite, Na_2SO_3, is allowed to stand exposed to oxygen or air, it changes spontaneously into *sodium sulphate*, Na_2SO_4.

$$2\,Na_2SO_3 + O_2 = 2\,Na_2SO_4$$

Insoluble Sulphites. *Some insoluble sulphites may be made as precipitates by adding suitable reagents to solutions of the alkali sulphites.* Calcium chloride, $CaCl_2$, and other soluble calcium salts produce in solutions of the soluble sulphites such as sodium sulphite, Na_2SO_3, white *calcium sulphite*, $CaSO_3$.

$$Na_2SO_3 + CaCl_2 = \mathbf{CaSO_3} + 2\,NaCl$$

Barium salts precipitate in sulphite solutions white *barium sulphite*, $BaSO_3$.

$$Na_2SO_3 + BaCl_2 = \mathbf{BaSO_3} + 2\,NaCl$$

Lead acetate, $Pb(C_2H_3O_2)_2$, and other soluble lead salts when added to a solution of a sulphite precipitate white *lead sulphite*, $PbSO_3$.

$$Na_2SO_3 + Pb(C_2H_3O_2)_2 = \mathbf{PbSO_3} + 2\,Na(C_2H_3O_2)$$

Silver nitrate, $AgNO_3$, and other soluble silver salts precipitate in a solution of a sulphite white *silver sulphite*, Ag_2SO_3.

$$Na_2SO_3 + 2\,AgNO_3 = \mathbf{Ag_2SO_3} + 2\,NaNO_3$$

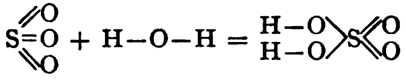
The precipitate turns gray when boiled in water, with the formation of silver in finely divided condition.

$$Ag_2SO_3 + H_2O = H_2SO_4 + 2\,Ag$$

Action of Acids upon Sulphites. *The stronger acids decompose sulphites with evolution of sulphur dioxide and formation of salts of the respective acids.* When sodium sulphite, Na_2SO_3, or sodium

Sulphuric Acid. *Dihydroxyl sulphuric acid, known ordinarily as sulphuric acid, the most stable hydroxide of sulphur, may be formed by the combination of sulphur trioxide with water, or by the oxidation of sulphurous acid.*

When sulphur trioxide is exposed to damp air, it forms heavy white fumes which consist of sulphuric acid in the condition of small liquid globules. Sulphur trioxide combines energetically with water, and from the solution nearly pure *sulphuric acid*, H_2SO_4, may be obtained by evaporation.



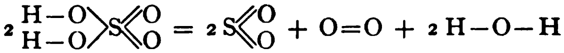
With methods for making sulphuric acid from sulphurous acid we have become acquainted in our study of the oxidation of the latter acid.

The *sulphuric acid* obtained in these ways is a colorless, oily liquid, containing about 98.5 per cent. of anhydrous sulphuric acid of the composition H_2SO_4, and about 1.5 per cent. of water, having a specific gravity of 1.84 at 15°, and distilling at 338°. This is the ordinary *concentrated sulphuric acid* of commerce, obtained by condensing the last two thirds of the distillate from more dilute water solutions obtained in the manufacturing processes. Pure solid *anhydrous sulphuric acid*, of the composition H_2SO_4, melting at 10.5°, may be obtained as white crystals by repeatedly crystallizing the concentrated sulphuric acid, at $-35°$ for the first crop of crystals, and between 0° and 10° after some crystals have been obtained with which to start a new crystallization. Dilute *sulphuric acid solutions* containing large proportions of water have a sour taste, turn the color of vegetable dyes, and are readily decomposed by the electric current, and by many metals, with the evolution of hydrogen.

Hydrates of Sulphuric Acid. Sulphuric acid has a strong attraction for water, as is shown by the rise of temperature observed when concentrated sulphuric acid and water are mixed, and by the fact that the mixtures of the concentrated acid with water when cooled again to the ordinary temperature occupy less volume than the sum of the original volumes of acid and water. Further examination of the action shows that *by the combination of water with sulphuric acid definite hydrates are produced.* A definite hydrate is obtained when a solution containing 85 per cent. of sulphuric acid and 15 per cent. of water is cooled to 0°. Under these conditions large six-sided prisms are obtained, of the composition acid upon sugar and starch and cellulose. Vegetable tissues, such as wood and cotton, and vegetable products, such as paper and textile fabrics, may be destroyed by the corrosive action of sulphuric acid. Animal tissues, such as the skin and mucous membrane, are quickly destroyed by sulphuric acid, which is therefore a powerful corrosive poison. By acting upon paper with sulphuric acid already mixed with some water, a tough *parchment paper* may be made.

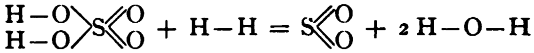
Reduction of Sulphuric Acid.

Sulphuric acid may be reduced by the dissociating action of heat as well as by suitable agents having a high affinity for oxygen. Passed through red-hot tubes or vessels of earthenware, sulphuric acid is decomposed into sulphur dioxide, oxygen, and water.

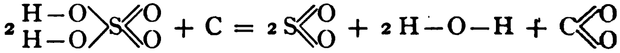


$$2\begin{matrix}\mathrm{H-O}\\ \mathrm{H-O}\end{matrix}\!>\!\mathrm{S}\!<\!\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix} = 2\,\mathrm{S}\!<\!\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix} + \mathrm{O{=}O} + 2\,\mathrm{H-O-H}$$

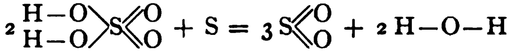
Hydrogen, carbon, and sulphur reduce boiling concentrated sulphuric acid to sulphur dioxide and water.



$$\begin{matrix}\mathrm{H-O}\\ \mathrm{H-O}\end{matrix}\!>\!\mathrm{S}\!<\!\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix} + \mathrm{H-H} = \mathrm{S}\!<\!\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix} + 2\,\mathrm{H-O-H}$$

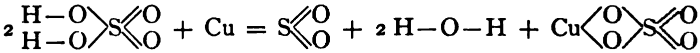


$$2\begin{matrix}\mathrm{H-O}\\ \mathrm{H-O}\end{matrix}\!>\!\mathrm{S}\!<\!\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix} + \mathrm{C} = 2\,\mathrm{S}\!<\!\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix} + 2\,\mathrm{H-O-H} + \mathrm{C}\!<\!\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}$$

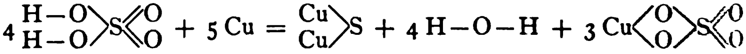


$$2\begin{matrix}\mathrm{H-O}\\ \mathrm{H-O}\end{matrix}\!>\!\mathrm{S}\!<\!\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix} + \mathrm{S} = 3\,\mathrm{S}\!<\!\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix} + 2\,\mathrm{H-O-H}$$

Copper effects a similar reduction of boiling concentrated sulphuric acid, cupric sulphate, $CuSO_4$, or cuprous sulphide, Cu_2S, being formed among the products of the action.



$$2\begin{matrix}\mathrm{H-O}\\ \mathrm{H-O}\end{matrix}\!>\!\mathrm{S}\!<\!\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix} + \mathrm{Cu} = \mathrm{S}\!<\!\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix} + 2\,\mathrm{H-O-H} + \mathrm{Cu}\!<\!\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\!>\!\mathrm{S}\!<\!\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}$$



$$4\begin{matrix}\mathrm{H-O}\\ \mathrm{H-O}\end{matrix}\!>\!\mathrm{S}\!<\!\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix} + 5\,\mathrm{Cu} = \begin{matrix}\mathrm{Cu}\\ \mathrm{Cu}\end{matrix}\!>\!\mathrm{S} + 4\,\mathrm{H-O-H} + 3\,\mathrm{Cu}\!<\!\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\!>\!\mathrm{S}\!<\!\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}$$

The action of mercury upon concentrated sulphuric acid is similar to that of copper.

Although we cannot prepare hydrogen in quantity by acting upon sulphuric acid with copper, it is conceivable that the reaction between the two substances consists in the setting free of hydrogen which at the moment of its liberation reduces some of the excess of sulphuric acid, forming sulphur dioxide in the first case, and in the second case sulphur.

From sodium hydroxide by neutralization with sulphuric acid, the neutral *sodium sulphate*, Na_2SO_4, or the acidic *sodium hydrogen sulphate*, $NaHSO_4$, may be obtained.

$$\mathit{H}_2\mathrm{SO}_4 + 2\,\mathit{Na}\mathrm{OH} = \mathit{Na}_2\mathrm{SO}_4 + 2\,\mathrm{H_2O}$$
$$\mathit{H}\mathrm{HSO}_4 + \mathit{Na}\mathrm{OH} = \mathit{Na}\mathrm{HSO}_4 + \mathrm{H_2O}$$

By the action of sulphuric acid upon zinc carbonate, $ZnCO_3$, *zinc sulphate*, $ZnSO_4$, is produced.

$$\mathit{Zn}\mathrm{CO}_3 + \mathit{H}_2\mathrm{SO}_4 = \mathit{Zn}\mathrm{SO}_4 + \mathrm{H_2O} + \mathrm{CO_2}$$

Zinc sulphite, $ZnSO_3$, is acted upon by sulphuric acid in similar manner, *zinc sulphate* and sulphur dioxide being formed.

$$\mathit{Zn}\mathrm{SO}_3 + \mathit{H}_2\mathrm{SO}_4 = \mathit{Zn}\mathrm{SO}_4 + \mathrm{H_2O} + \mathrm{SO_2}$$

By heating nitrates, chlorides, and many other salts of volatile acids with sulphuric acid, sulphates may be produced, while the volatile acids formed may be separated by distillation. With sodium nitrate, $NaNO_3$, sulphuric acid gives nitric acid, HNO_3, and with sodium chloride, NaCl, it gives hydrochloric acid, HCl, the neutral *sodium sulphate*, or acidic *sodium hydrogen sulphate* being also formed.

$$2\,\mathit{Na}\mathrm{NO}_3 + \mathit{H}_2\mathrm{SO}_4 = \mathit{Na}_2\mathrm{SO}_4 + 2\,\mathrm{HNO_3}$$
$$2\,\mathit{Na}\mathrm{Cl} + \mathit{H}_2\mathrm{SO}_4 = \mathit{Na}_2\mathrm{SO}_4 + 2\,\mathrm{HCl}$$

Insoluble Sulphates. *Some insoluble sulphates are formed as precipitates by the action of sulphuric acid or of soluble sulphates upon suitable hydroxides or salts.* A soluble barium compound, such as barium hydroxide, $Ba(OH)_2$, or barium chloride, $BaCl_2$, will form immediately in a dilute solution of sulphuric acid or a sulphate, such as sodium sulphate, Na_2SO_4, a precipitate of white *barium sulphate*, $BaSO_4$, which is not acted upon by acids.

$$\mathrm{H_2SO_4} + \mathrm{Ba(OH)_2} = \mathbf{BaSO_4} + 2\,\mathrm{H_2O}$$
$$\mathrm{Na_2SO_4} + \mathrm{Ba(OH)_2} = \mathbf{BaSO_4} + 2\,\mathrm{NaOH}$$
$$\mathrm{H_2SO_4} + \mathrm{BaCl_2} = \mathbf{BaSO_4} + 2\,\mathrm{HCl}$$
$$\mathrm{Na_2SO_4} + \mathrm{BaCl_2} = \mathbf{BaSO_4} + 2\,\mathrm{NaCl}$$

A soluble strontium compound, such as strontium nitrate, $Sr(NO_3)_2$, will produce slowly in sufficiently concentrated solutions of sulphuric

Na_2S, is placed on the surface of a piece of silver, and moistened with water, a characteristic black stain of silver sulphide, Ag_2S, is formed.

$$Na_2S + 2\,Ag + 2\,H_2O = Ag_2S + 2\,NaOH + H_2$$

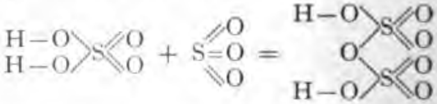
When barium sulphate, $BaSO_4$, which is insoluble in water, is heated with carbon and sodium carbonate, barium carbonate and the soluble sodium sulphate are first formed, and the sodium sulphate is subsequently reduced to sodium sulphide, Na_2S.

$$BaSO_4 + Na_2CO_3 = BaCO_3 + Na_2SO_4$$

These reactions are employed in testing substances for the presence of sulphates, the substances being mixed with powdered charcoal and sodium carbonate, placed in a shallow cavity in a piece of charcoal, and heated strongly by means of a blowpipe, the fused residue being subsequently placed on silver and moistened, the production of the black stain of silver sulphide being taken as an indication of the presence of a sulphate in the original substance.

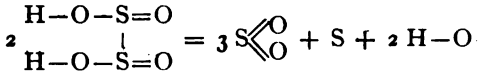
Under the action of heat some sulphates are readily dissociated into their component oxides, and some are not thus dissociated. The alkali sulphates, such as sodium sulphate, Na_2SO_4, and the alkali earth sulphates, such as barium sulphate, $BaSO_4$, are not dissociated into the component oxides at red heat, though the sulphates of copper, zinc, iron, and other similar elements, may be thus decomposed.

Disulphuric Acid. *From sulphuric acid and sulphur trioxide another acid, disulphuric acid, of which sulphur trioxide is likewise the anhydride, may be made.* Sulphur trioxide, SO_3, is readily absorbed by sulphuric acid, forming a heavy strongly fuming liquid from which white crystals of the instable *disulphuric acid*, $H_2S_2O_7$ (pyrosulphuric acid), may be separated on cooling.



The crystals melt at 35°. They fume strongly in the air, decomposing spontaneously with evolution of sulphur trioxide and the formation of sulphuric acid. Both disulphuric acid and the *Nordhausen sulphuric acid* (fuming sulphuric acid), which is sulphuric acid containing disulphuric acid, formerly made in large quantities by heating ferrous sul-

Hyposulphurous acid is acted upon easily by the ox and serves as a strong reducing agent. It is unstabl spontaneously into sulphur dioxide, sulphur, and water.



$$2\ \begin{matrix}H-O-S=O\\ |\\ H-O-S=O\end{matrix} = 3\,S\begin{matrix}O\\ O\end{matrix} + S + 2\,H-O$$

Sodium hyposulphite, $Na_2S_2O_4$, which is more stable th phurous acid, may be formed by the action of zinc fili hydrogen sulphite, $NaHSO_8$, or by the electrolysis of th crystals of the composition $Na_2S_2O_4 \cdot 2\,H_2O$.

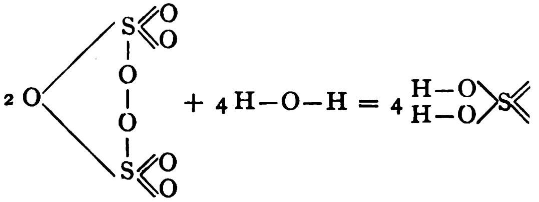
$$4\,NaHSO_3 + Zn = Na_2S_3O_4 + Na_2SO_3 + ZnSO$$

Sodium hyposulphite is decomposed by sulph formation of sulphur dioxide, sulphur, water, and sodiun

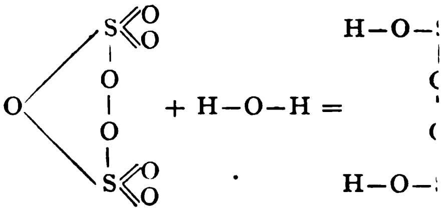
$$2\,Na_2S_2O_4 + 2\,H_2SO_4 = 3\,SO_2 + S + 2\,H_2O +$$

Though disulphur trioxide, S_2O_3, corresponds in co anhydride of hyposulphurous acid, the action of this is so violent that the acid if formed is at once decompo

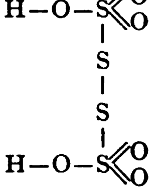
Persulphuric Acid. *Persulphuric acid*, $H_2S_2O_8$, has a compos ing to that of its anhydride, sulphur When water is added directly to sulphur heptoxi lence of the action is such that sulphuric acid is forme liberated, persulphuric acid being unstable under these



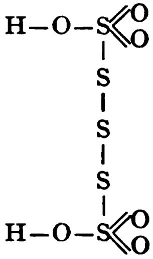
When, however, sulphur heptoxide is added to solution of sulphuric acid in water, the violence of th water is so moderated that persulphuric acid remains i



Tetrathionic acid,

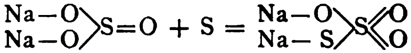


Pentathionic acid,



Thiosulphates. *The thiosulphates, salts of the unstable thiosulphuric acid, may be obtained by many reactions which involve directly or indirectly the combination of a metal, oxygen, and sulphur in certain definite proportions.*

Sodium Thiosulphate. *Sodium thiosulphate,* $Na_2S_2O_3 \cdot 5\ H_2O$, large colorless crystals, easily efflorescent in dry air, may be made by boiling a solution of sodium sulphite, Na_2SO_3, with finely divided sulphur, and crystallizing the salt from the filtered liquid,



$$\begin{matrix}Na-O\\Na-O\end{matrix}\!\!>S=O + S = \begin{matrix}Na-O\\Na-S\end{matrix}\!\!>S\!\!<\begin{matrix}O\\O\end{matrix}$$

or by the oxidation of the sodium sulphides, Na_2S, or Na_2S_5, by the oxygen of the air,

$$2\ Na_2S + 2\ O_2 + H_2O = Na_2S_2O_3 + 2\ NaOH$$

$$2\ Na_2S_5 + 3\ O_2 = 2\ Na_2S_2O_3 + 6\ S$$

or by sulphurous acid,

$$2\ Na_2S + 3\ H_2SO_3 = 2\ Na_2S_2O_3 + 3\ H_2O + S$$

or by sodium sulphite, Na_2SO_3, or some other sulphite, in the presence of iodine,

$$Na_2S + Na_2SO_3 + I_2 = Na_2S_2O_3 + 2\ NaI$$

or by weak oxidizers generally.

When sodium thiosulphate is heated with sodium carbonate, Na_2CO_3, and carbon, sodium monosulphide, Na_2S, and carbon dioxide are formed.

$$Na_2S_2O_3 + Na_2CO_3 + 3\,C = 2\,Na_2S + 3\,CO_2$$

Though the thiosulphates are fairly stable salts, the *thiosulphuric acid*, $H_2S_2O_3$, presumably formed from them in solution by the action of stronger acids, decomposes spontaneously.

Action of Acids upon Thiosulphates.

By the action of acids upon thiosulphates in solution, sulphurous acid is formed and sulphur is set free. When sulphuric acid acts upon sodium thiosulphate, $Na_2S_2O_3$, solid sulphur is set free, while sulphurous acid, H_2SO_3, and sodium sulphate remain in solution,

$$Na_2S_2O_3 + H_2SO_4 = H_2SO_3 + S + Na_2SO_4$$

and similarly hydrochloric acid gives sulphurous acid, sulphur, and sodium chloride.

$$Na_2S_2O_3 + 2\,HCl = H_2SO_3 + S + 2\,NaCl$$

The action of acetic acid and of carbonic acid upon sodium thiosulphate is similar to the action of sulphuric acid and of hydrochloric acid. Exposure of solutions of thiosulphates to the carbon dioxide of the air is sufficient to bring about slowly and after some time a similar decomposition.

Oxidation of Thiosulphates.

The thiosulphates are readily oxidized by direct oxidizing agents, and indirectly in the presence of water by free chlorine, bromine, and iodine, and so are capable of acting as reducers.

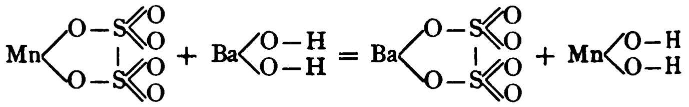
Strong oxidizing agents convert thiosulphates into sulphates; weaker ***oxidizing agents produce the tetrathionates as immediate products.*** Thus, when potassium permanganate, $KMnO_4$, or permanganic acid, $HMnO_4$, and sodium thiosulphate, $Na_2S_2O_3$, interact in the presence of sulphuric acid, the oxidizing action converts the thiosulphate to sodium sulphate, and the reducing effect is manifested in the formation of a manganese compound in which the valence of manganese is lower than its valence in the original compound.

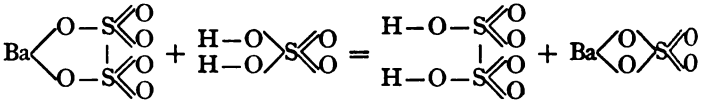
$$8\,HMnO_4 + 5\,Na_2S_2O_3 + 3\,H_2SO_4 = 8\,MnSO_4 + 5\,Na_2SO_4 + 7\,H_2O$$

A solution of chromic acid, H_2CrO_4, containing another free acid, is similarly acted upon by sodium thiosulphate.

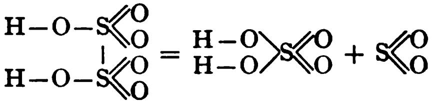
On the other hand, when an acidulated solution of a ferric salt, such as ferric chloride, $FeCl_3$, and sodium thiosulphate are brought together, the reducing action of the thiosulphate is shown similarly by the formation of a compound in which iron has a lower valence, but the oxidizing action proceeds to the intermediate point of the formation of sodium tetrathionate, $Na_2S_4O_6$.

With the manganese dithionate some manganous sulphate is simultaneously produced. By the action of barium hydroxide, $Ba(OH)_2$, upon manganese dithionate, *barium dithionate*, BaS_2O_6, is formed. and when this is heated with sulphuric acid, barium sulphate, $BaSO_4$, is precipitated, leaving a dilute solution of dithionic acid.

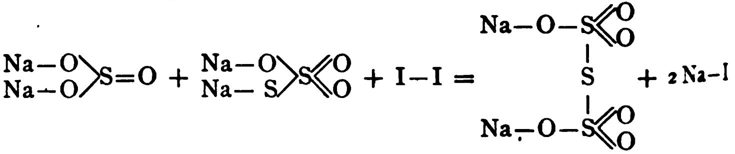




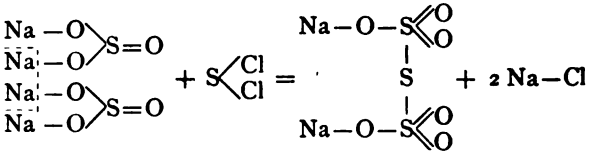
The solution of dithionic acid may be somewhat concentrated, but finally decomposes into sulphuric acid and sulphur dioxide.



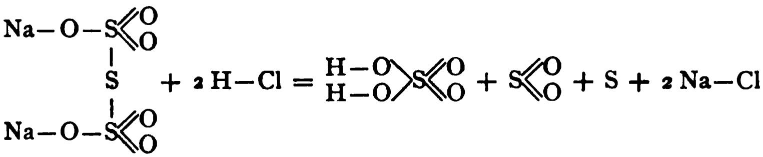
Trithionic acid, $H_2S_3O_6$, is unstable, but *sodium trithionate*, $Na_2S_3O_6$, may be produced by acting with iodine upon a mixture of sodium sulphite, Na_2SO_3, and sodium thiosulphate, $Na_2S_2O_3$, sodium iodide also being formed.



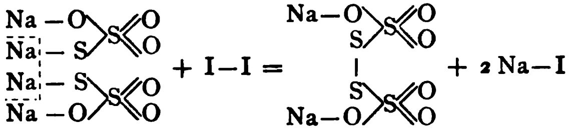
Sodium trithionate may also be produced when sodium sulphite, Na_2SO_3, and sulphur dichloride, SCl_2, interact.



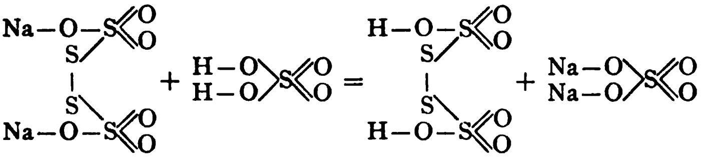
The action of hydrochloric acid upon sodium trithionate results in the formation of sulphuric acid, sulphur dioxide and sulphur, with sodium chloride, by decomposition of the unstable trithionic acid first formed.



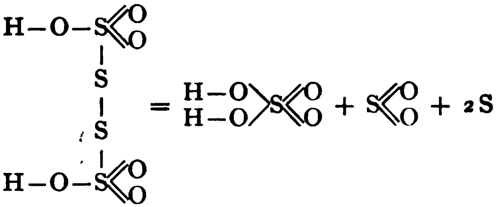
Tetrathionic acid, $H_2S_4O_6$, may be obtained in solution from *sodium tetrathionate*, $Na_2S_4O_6$, which, as has already been shown, is formed when iodine acts upon sodium thiosulphate, $Na_2S_2O_3$.



The solution obtained by acting upon sodium tetrathionate with sulphuric acid contains tetrathionic acid and sodium sulphate.



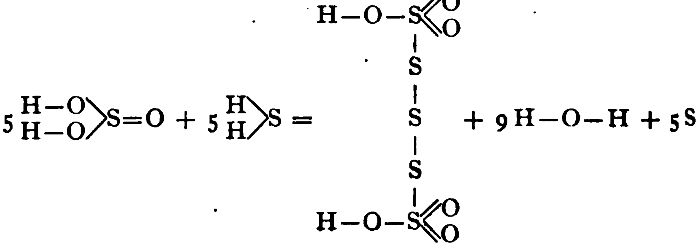
The tetrathionic acid is fairly stable in dilute solutions only, and when concentrated breaks up into sulphuric acid, sulphur dioxide, and sulphur.



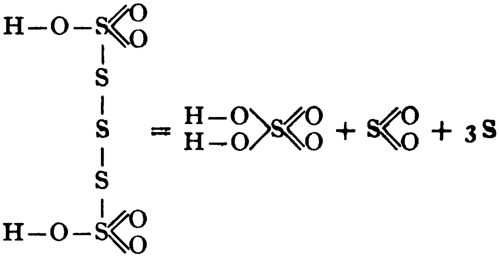
Tetrathionic acid is one of the products of the reducing action of hydrogen sulphide, H_2S, upon sulphurous acid, H_2SO_3, and by neutralizing with a suitable base the solution thus obtained a corresponding tetrathionate may be formed.

$$4\,H_2SO_3 + 3\,H_2S = H_2S_4O_6 + 6\,H_2O + 3\,S$$

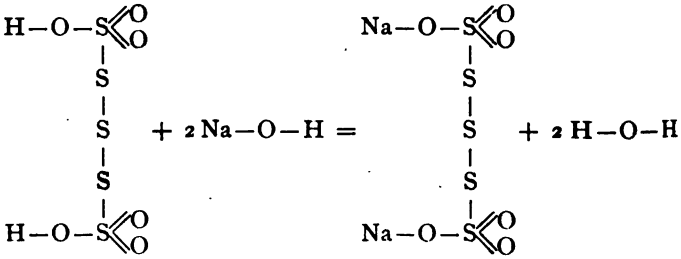
Pentathionic acid, $H_2S_5O_6$, is likewise produced in solution by the action of hydrogen sulphide upon sulphurous acid.



Pentathionic acid decomposes readily into sulphuric acid, sulphur dioxide, and sulphur.



From a solution of pentathionic acid *sodium pentathionate*, $Na_2S_5O_6$ may be prepared by neutralizing with sodium hydroxide.



This and other similar pentathionates are readily decomposed by acids.

Sulphides.

By the direct combination of elements with sulphur many sulphides may be formed. When copper is heated strongly with finely divided sulphur, a black mass of *cuprous sulphide*, Cu_2S, is formed, while iron in a similar manner gives with sulphur black porous *ferrous sulphide*, FeS.

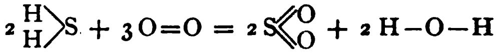
$$2Cu + S = Cu_2S$$

$$Fe + S = FeS$$

We may make hydrogen combine to some extent with sulphur to form hydrogen sulphide by passing hydrogen through boiling sulphur, or by heating together hydrogen and sulphur to 500°. We have already noted several instances of the formation of hydrogen sulphide as one of the products of the reduction of sulphuric acid, or other acids of sulphur, by certain elements.

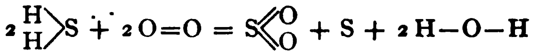
Hydrogen sulphide, H_2S (hydrosulphuric acid), is a colorless gas, of strong characteristic odor, having a specific gravity of 34, moderately soluble in water. At ordinary temperature, under a pressure of 17 atmospheres, it forms a colorless liquid of specific gravity 0.9, which boils at −63.5° under ordinary pressure, and forms a white solid at −91°. Hydrogen sulphide has a poisonous effect on both animals and plants, although the growth of some microörganisms does not seem to be retarded by it. Hydrogen sulphide is sometimes found present in volcanic gases, and in the atmosphere in regions where it has been formed by the incomplete burning of coal or other sulphur-containing fuels, or by the decay of organic matter containing sulphur. It is largely used as a reagent in the laboratory.

Oxidation of Hydrogen Sulphide. *Hydrogen sulphide may be readily oxidized in air or oxygen, and it reduces many compounds by removing oxygen or other elements from them.* In the presence of oxygen or air, hydrogen sulphide, H_2S, burns with a pale blue flame, forming sulphur dioxide, SO_2, and water.



$$2\,{}^{H}_{H}\!>\!S + 3\,O{=}O = 2\,S\!<\!{}^{O}_{O} + 2\,H{-}O{-}H$$

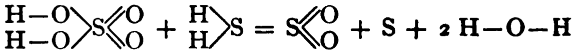
In less than an excess of oxygen the oxidation may be but partial, resulting in the separation of sulphur.



$$2\,{}^{H}_{H}\!>\!S + 2\,O{=}O = S\!<\!{}^{O}_{O} + S + 2\,H{-}O{-}H$$

A water solution of hydrogen sulphide is decomposed slowly by the oxygen of the air with separation of sulphur.

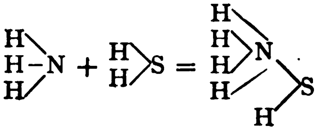
Hydrogen sulphide will reduce hot concentrated sulphuric acid, with the formation of sulphur dioxide, SO_2, sulphur, and water.



$$^{H-O}_{H-O}\!>\!S\!<\!{}^{O}_{O} + {}^{H}_{H}\!>\!S = S\!<\!{}^{O}_{O} + S + 2\,H{-}O{-}H$$

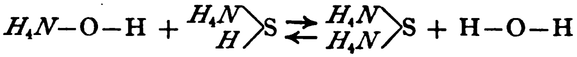
Arsenic acid, H_3AsO_4, iodic acid, HIO_3, chloric acid, $HClO_3$, and other acids may be similarly reduced by hydrogen sulphide.

This substance may be also crystallized out by passing hydrogen sulphide into a solution of ammonia gas in alcohol.



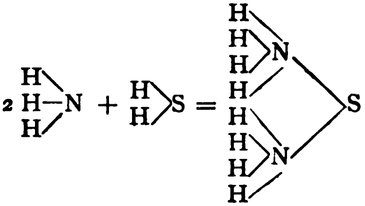
$$H_3N + H_2S = H_4N{-}S{-}H$$

The addition of an excess of ammonium hydroxide to the solution of ammonium hydrogen sulphide tends to form ***ammonium sulphide***, $(NH_4)_2S$, which, however, is easily hydrolyzed in the reversed reaction.



$$H_4N{-}O{-}H + \begin{matrix} H_4N \\ H \end{matrix}\!\!>\!S \rightleftarrows \begin{matrix} H_4N \\ H_4N \end{matrix}\!\!>\!S + H{-}O{-}H$$

Ammonium sulphide may be isolated in crystalline condition by mixing one volume of hydrogen sulphide with two volumes of ammonia gas at — 18°.



$$2\,H_3N + H_2S = (H_4N)_2S$$

Ammonium sulphide dissociates at ordinary temperatures into ammonia and ammonium hydrogen sulphide, and the latter compound breaks up at 45° into ammonia and hydrogen sulphide.

The solution of ammonium sulphide in ammonium hydroxide will dissolve finely divided sulphur to form ammonium polysulphides, and this solution is known as *yellow ammonium sulphide.* By the action of the air the ordinary solution of ammonium sulphide tends to form yellow ammonium sulphide.

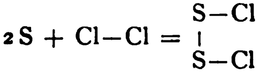
Insoluble Sulphides.

Many insoluble sulphides may be formed as characteristic precipitates by adding hydrogen sulphide, ammonium sulphide, or other soluble sulphide to solutions of salts. Thus, when hydrogen sulphide, H_2S, or ammonium sulphide, $(NH_4)_2S$, is added to a solution of a silver salt, such as silver nitrate, $AgNO_3$, a precipitate of black *silver sulphide*, Ag_2S, acted upon by dilute acids or by an excess of the reagent, is formed.

the insoluble liquid carbon disulphide, which is manu some useful purposes, and the insoluble arsenic sulph minerals and are also of value. The sulphides of so and of the other alkali elements may be obtained as d such as $Na_2S \cdot 6\ H_2O$, $2\ KHS \cdot H_2O$, which are v solutions of the alkali sulphides are heated with fin various *polysulphides* are formed, such as Na_2S_2, Na_2S taining high proportions of sulphur. Similar polys and of other alkali earth elements are known. By t acid, such as hydrochloric acid, upon polysulphides tions, the unstable *hydrogen pentasulphide*, H_2S_5, i yellow, oily liquid, of specific gravity 1.7, readil hydrogen sulphide and sulphur. We have already *of sulphur* used in medicine, which consists of finely in suspension, formed by acting upon solutions o acids. The insoluble metal sulphides, the more im have mentioned, form an important class of minera dantly and widely distributed in the world, and a pure metals which may be reclaimed from them. ores are strongly heated in the air, the sulphur in t oxidized than are the metals, and when such or proper condition with carbon or some other redu possible to completely burn away the sulphur, leavi various *metallurgical operations* which depend up sulphides will be studied in connection with the in selves. Many of the mineral sulphides are valuabl

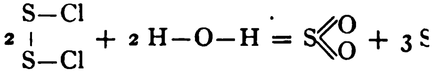
Compounds of Sulphur and Chlorine.

Sulphur combines with chlorine for chlorides. When chlorine gas is sulphur, *sulphur monochloride*, S_2Cl_2, of specific gravity 135, which may be condensed sharp-smelling liquid, of specific gravity 1.68, boili



$$2\,S + Cl{-}Cl = \begin{array}{l} S{-}Cl \\ | \\ S{-}Cl \end{array}$$

The liquid fumes strongly in damp air and is deco sulphur dioxide, SO_2, sulphur, and hydrochloric ac



$$2\begin{array}{l} S{-}Cl \\ | \\ S{-}Cl \end{array} + 2\,H{-}O{-}H = S\begin{array}{l} {=}O \\ {=}O \end{array} + 3\,S$$

Summary. *We note, in regard to the sulphur compounds, that sulphur dioxide is a colorless gas, soluble in water, forming the unstable sulphurous acid in solution; that sulphur trioxide, a colorless liquid or white solid, combines with water to form the colorless liquid dihydroxylsulphuric acid, known as common sulphuric acid, and its hydrates; and with sulphuric acid to form the crystalline disulphuric acid: that disulphurtrioxide, a rare oxide, although corresponding to hyposulphurous acid in composition, does not form that acid by action upon water, owing to the violence of the reaction; that sulphur heptoxide, another rare oxide, may act upon water under proper conditions to form unstable persulphuric acid in solution.*

Sulphurous acid may be oxidized to sulphuric acid; it forms neutral and acidic sulphites, solids, readily oxidized to sulphates, and decomposed by heating and by acids. The alkali sulphites are soluble; some other sulphites are insoluble.

Sulphuric acid may be reduced to sulphurous acid, and may be decomposed by heating; it may be oxidized to persulphuric acid; it forms neutral and acidic sulphates, those of the alkalies being white and soluble, others being insoluble and variously colored. Some sulphates may be decomposed by heating.

From acidic sulphites, the disulphites may be formed spontaneously, and hyposulphites by reduction; by heating acidic sulphates, disulphates are formed; by oxidizing sulphates, persulphates may be obtained.

Corresponding to the respective thioacids, which exist only in solution, there are the thiosalts: the thiosulphates, made by the action of sulphur upon sulphites, and by the oxidation of sulphides; and the polythionates, made in various ways, — all being unstable, readily decomposed by acids. The alkali thiosulphates are soluble, and may be oxidized to tetrathionates or to sulphates; some thiosulphates are insoluble.

The sulphides of the alkali elements and the ammonium sulphides are soluble, while those of the heavier metals are insoluble. The gaseous hydrogen sulphide, formed by acting upon suitable sulphides of metals with acids, as well as other soluble sulphides, will precipitate some insoluble sulphides from solutions of suitable compounds in presence of acids, but some sulphides are acted upon by an excess of soluble sulphides with formation of sulphosalts. The sulphides may be readily oxidized. Sulphur forms several binary compounds with chlorine, also several compounds with chlorine and oxygen.

The excess of sulphur dioxide and oxygen in the chamber may assist the water in decomposing the nitrosyl sulphuric acid with formation of sulphuric acid and nitrogen trioxide,

$$4\,H(NO)SO_4 + 2\,SO_2 + O_2 + 4\,H_2O = 6\,H_2SO_4 + 2\,N_2O_3$$

or sulphur dioxide and water alone may effect the decomposition, with separation of nitrogen dioxide, which in an excess of oxygen may be used up in making more nitrosyl sulphuric acid.

$$2\,H(NO)SO_4 + SO_2 + 4\,H_2O = 3\,H_2SO_4 + 2\,NO$$
$$4\,SO_2 + 4\,NO + 3\,O_2 + 2\,H_2O = 4\,H(NO)SO_4$$

In a deficiency of oxygen, however, the nitrogen monoxide may remain mixed with the sulphuric acid in unchanged condition.

"Chamber Crystals."

When, owing to a deficiency of water or to a condition of low temperature, the nitrosyl sulphuric acid is not immediately decomposed, it may collect on the lead walls as the so-called *chamber crystals*, which may be decomposed by water with the formation of sulphuric acid, nitrogen tetroxide, and nitrogen dioxide.

$$4\,H(NO)SO_4 + 2\,H_2O = 4\,H_2SO_4 + 2\,NO_2 + 2\,NO$$

The formation of chamber crystals may, however, be prevented by providing a suitable excess of nitrogen trioxide and steam, and keeping the mixed gases at sufficiently high temperature.

It is possible, moreover, that nitrogen tetroxide, NO_2, introduced into the lead chambers with the nitrogen trioxide, or formed in the chambers by the decomposition of nitrogen trioxide at the prevailing high temperature, or by the decomposition of "chamber crystals," may act similarly to nitrogen trioxide in the oxidation of sulphur dioxide and the consequent formation of sulphuric acid.

We know that nitric acid may oxidize sulphur dioxide in presence of water, forming sulphuric acid and nitrogen trioxide.

$$2\,SO_2 + 2\,HNO_3 + H_2O = 2\,H_2SO_4 + N_2O_3$$

This reaction may occur in two stages, with the formation of nitrosyl sulphuric acid as an intermediate product. In the chamber process the nitrogen trioxide needed is formed by acting upon sodium nitrate with sulphuric acid and passing the resulting nitric acid vapors into the mixture of sulphur dioxide and steam before they enter the lead chambers. Sometimes, however, instead of decomposing sodium nitrate, liquid nitric acid is added to the mixed gases before they enter the lead chambers, or is injected into the chambers as a fine spray. It usually happens, therefore, that some sulphuric acid is formed by the action of nitric acid upon the mixed gases before the latter enter the lead chambers.

Under proper conditions — the presence of water and oxygen in sufficient excess and the attainment of a high enough temperature — some fuel is necessary, although with poorer ores fuel is supplied. In case pure sulphur is employed, the oxidation takes place in simple retorts or shallow trays placed in brick ovens. The *niter pot*, a small cast-iron vessel in which the nitric acid, from which the nitrogen oxides are to be generated, is formed from sodium nitrate by the action of sulphuric acid, is usually placed in one of the furnaces, or in a part of the flue heated by the fire, or sometimes in a separate furnace.

Glover Tower. The hot "burner gases," consisting of sulphur dioxide, oxygen, and sometimes of nitrogen trioxide or other nitrogen compounds, pass from the burners into the bottom of the *Glover tower* — a narrow chamber of lead 20 or 30 feet in height — through which the gases pass, coming in contact, during their rise, with a descending stream of dilute sulphuric acid by which they are cooled to 50° or 60°. In the Glover tower the gases receive some steam by evaporation from the dilute sulphuric acid, and in some cases, when no niter pots are employed, liquid nitric acid is introduced into the Glover tower with the sulphuric acid. It has already been shown that some sulphuric acid may be formed in the Glover tower by the action of nitric acid upon the burner gases, with the liberation of nitrogen trioxide.

Lead Chambers. From the Glover tower the cooled gases pass into the *lead chambers*, of which there are from three to five, the largest, which may have a capacity of 80,000 cu. ft. or more, being first in the series. The bottoms of the chambers consist of large lead pans, with vertical sides extending up a few inches outside the walls of the chambers in such a manner that the liquid which collects in the pans will form a hydraulic seal against the escape of the gases in the chambers. In these chambers the principal reactions, which we have discussed, take place. If sufficient steam is not furnished by evaporation in the Glover tower, jets of steam are injected directly into the lead chambers, while in some plants liquid nitric acid is similarly introduced as a fine spray. The crude dilute "chamber acid," of specific gravity never greater than 1.5–1.6, is drawn off from the chambers into shallow *lead pans*, in which it is concentrated by evaporation until a specific gravity of 1.71 is reached, after which it may be further concentrated in *platinum stills*, until the commercial concentrated "oil of vitriol," of specific gravity 1.84, is obtained. A portion of the chamber acid may be pumped to a reservoir at the top of the Glover tower, where it is used to dilute the stronger impure acid pumped from the Gay-Lussac tower in another part of the plant.

Gay-Lussac Tower. From the lead chambers the residual gases, consisting largely of nitrogen trioxide, and also containing nitrogen tetroxide, and in some cases lower nitrogen oxides, pass up through the *Gay-Lussac* tower, which is a narrow structure of lead or earthenware which may extend as high as 50 feet, and is filled with hard coke, over which a stream of concentrated sulphuric acid of specific dioxide with one volume of oxygen, made by decomposing pure concentrated sulphuric acid by heat and removing the water, was passed through tubes containing platinized asbestos, and the resulting sulphur trioxide collected by itself or passed into water or sulphuric acid. This process, owing to the cost of the sulphuric acid required, was very expensive, and all attempts to utilize a cheaper source of sulphur dioxide, such as the burner gases obtained by roasting pyrite or sulphur, failed when practiced on a large scale, owing to the deleterious effects on the contact-mass of platinum of the minute traces of arsenic or other metals present in the gases. The recent discovery of a method by which the ordinary burner gases, purified by slow cooling, may be oxidized spontaneously by contact with platinized asbestos in tubes which are kept cool by the incoming gases, has made it possible to manufacture sulphur trioxide and fuming sulphuric acid at a much lower cost than heretofore, and may even be employed for the manufacture of ordinary concentrated sulphuric acid, thus superseding the older chamber process. In 1900 116,000 tons of sulphur trioxide were manufactured in Germany by the new contact process.

“Oil of Vitriol.” We have seen that certain sulphates may be decomposed by heating, with the liberation of sulphur oxides. Thus, ferrous sulphate, $FeSO_4$, may decompose into ferric oxide, Fe_2O_3, sulphur trioxide, SO_3, and sulphur dioxide, SO_2,

$$2\,FeSO_4 = Fe_2O_3 + SO_3 + SO_2$$

and ferric sulphate, $Fe_2(SO_4)_3$, may be decomposed into ferric oxide, Fe_2O_3, and sulphur trioxide, SO_3.

$$Fe_2(SO_4)_3 = Fe_2O_3 + 3\,SO_3$$

Hydrous ferrous sulphate, $FeSO_4 \cdot 7H_2O$ (green vitriol), forms when heated in air a basic ferric sulphate, such as $Fe_2S_2O_9$, and this when heated more strongly decomposes into ferric oxide, Fe_2O_3, and sulphur trioxide.

$$Fe_2S_2O_9 = Fe_2O_3 + 2\,SO_3$$

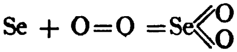
Since ancient times “Nordhausen sulphuric acid,” or “fuming sulphuric acid” (oil of vitriol), which consists of a mixture of disulphuric acid and sulphuric acid, has been prepared by heating partially dehydrated and oxidized “green vitriol” or “copperas.” At the present time small quantities of fuming sulphuric acid are made in Bohemia by heating basic ferric sulphate formed by the spontaneous oxidation of iron pyrites in air.

SELENIUM, Se, 79.2

Selenium is found combined chiefly as an impurity in *pyrite*, FeS_2, and other similar sulphides, and rarely in *selenides*, such as PbSe, HgSe, $Cu_2Se \cdot Ag_2Se$. When seleniferous sulphides are roasted to make

OXIDES	HYDROXIDES
Selenium dioxide, SeO_2	Selenious acid, H_2SeO_3 Selenic acid, H_2SeO_4

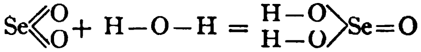
When strongly heated in oxygen or air, selenium burns with a bright blue flame, forming ***selenium dioxide***, SeO_2, as a vapor which condenses to form needlelike crystals, volatile at 320°.



$$\mathrm{Se + O{=}O = Se}\begin{matrix}\diagup O\\ \diagdown O\end{matrix}$$

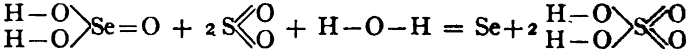
The presence of the least trace of organic matter, like the dust of ordinary air, is sufficient, however, to effect the reduction of elementary selenium from selenium dioxide, and for this reason selenium dioxide often turns red when sublimed, or exposed to ordinary air. The disagreeable odor, similar to that of decayed horse-radish, emitted by selenium dioxide vapor, is probably connected with the presence of finely divided selenium, or possibly of traces of hydrogen selenide, H_2Se, formed by the action of moisture.

Selenium dioxide dissolves in water, forming ***selenious acid***, H_2SeO_3, which may be obtained in crystalline form.



$$\mathrm{Se}\begin{matrix}\diagup O\\ \diagdown O\end{matrix} + \mathrm{H{-}O{-}H} = \begin{matrix}\mathrm{H{-}O}\diagdown\\ \mathrm{H{-}O}\diagup\end{matrix}\mathrm{Se{=}O}$$

Selenious acid, like selenium dioxide, is easily reduced, sulphur dioxide acting upon it with formation of sulphuric acid and a red colloidal solution of selenium, which on standing, and more quickly on heating, deposits brownish red amorphous selenium.

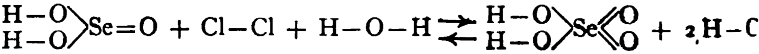


$$\begin{matrix}\mathrm{H{-}O}\diagdown\\ \mathrm{H{-}O}\diagup\end{matrix}\mathrm{Se{=}O} + 2\,\mathrm{S}\begin{matrix}\diagup O\\ \diagdown O\end{matrix} + \mathrm{H{-}O{-}H} = \mathrm{Se} + 2\begin{matrix}\mathrm{H{-}O}\diagdown\\ \mathrm{H{-}O}\diagup\end{matrix}\mathrm{S}\begin{matrix}\diagup O\\ \diagdown O\end{matrix}$$

Hydrogen sulphide decomposes selenious acid, H_2SeO_3, with formation of insoluble selenium sulphide, SeS, intermixed with sulphur.

Selenious acid neutralizes bases with formation of neutral selenites, or acidic selenites, and water. Thus, we have ***sodium selenite***, Na_2SeO_3, *sodium hydrogen selenite*, $NaHSeO_3$, and similar compounds of potassium and other elements. The selenites of the alkali elements are soluble in water.

By the oxidation of selenious acid, H_2SeO_3, or of selenites, by suitable agents, selenic acid, H_2SeO_4, may be obtained. Oxidation of selenious acid, H_2SeO_3, with consequent formation of ***selenic acid***, H_2SeO_4, in solution, may be brought about by passing chlorine into a water solution of selenious acid suitably dilute,



$$\begin{matrix}\mathrm{H{-}O}\diagdown\\ \mathrm{H{-}O}\diagup\end{matrix}\mathrm{Se{=}O} + \mathrm{Cl{-}Cl} + \mathrm{H{-}O{-}H} \rightleftarrows \begin{matrix}\mathrm{H{-}O}\diagdown\\ \mathrm{H{-}O}\diagup\end{matrix}\mathrm{Se}\begin{matrix}\diagup O\\ \diagdown O\end{matrix} + 2\,\mathrm{H{-}Cl}$$

nides may be formed by direct combination of elements with selenium, and may be decomposed by acids with formation of hydrogen selenide.

By the action of selenium upon chlorine, *selenium monochloride*, Se_2Cl_2, a brown, oily liquid, and *selenium tetrachloride*, $SeCl_4$, a light yellow solid, both of which are decomposed by water with formation of selenious acid, may be made. A *selenium oxychloride*, $SeOCl_2$, is also known, as are also similar selenium bromides and iodides, and oxybromides and oxyiodides. By the action of selenium upon sulphur trioxide, or upon concentrated sulphuric acid, green *selenium sulphur trioxide* may be formed.

TELLURIUM, Te, [127.6]

Tellurium is found in small amounts in free condition, and in combination with silver, gold, bismuth and other elements, in certain *tellurides*, such as Ag_2Te, $(AgAu)Te_2$, Bi_2Te_3, etc., and in other rare minerals. By treating tellurium ores with hydrochloric acid, and then oxidizing them with aqua regia, tellurous acid, H_2TeO_3, is formed, from which, after removing the compounds of gold or other elements by suitable reagents, the tellurium may be precipitated by the action of sulphur dioxide.

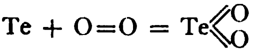
Tellurium as thus prepared is an amorphous black powder which when heated turns into a grayish white, lustrous crystalline mass, of specific gravity 6.24, insoluble in water and in carbon disulphide, melting at 452°, boiling at 1390°, with formation of a yellow vapor.

The specific gravity of tellurium vapor between 1400° and 1700° corresponds to an approximate molecular weight of 254, which suggests the molecular symbol Te_2.

Tellurium forms one oxide by direct combination of the element with oxygen, while two other oxides may be made indirectly, and two acidic hydroxides may be made by oxidizing tellurium.

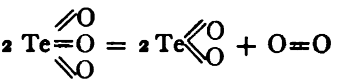
OXIDES	HYDROXIDES
Tellurium monoxide, TeO	
Tellurium dioxide, TeO_2	Tellurous acid, H_2TeO_3
Tellurium trioxide, TeO_3	Telluric acid, H_2TeO_4

When tellurium is sufficiently heated in oxygen or air, it burns with a blue flame with the formation of white vapors of *tellurium dioxide*, TeO_2, condensing to a white solid, volatile at red heat.



$$Te + O{=}O = Te\begin{matrix}{=}O\\{=}O\end{matrix}$$

Tellurous acid, H_2TeO_3 (tellurous hydroxide), corresponding to tellurium dioxide, may be obtained by oxidizing tellurium with nitric acid. Thus, when tellurium is acted upon by nitric acid, and the resulting which upon further heating decomposes into tellurium dioxide, TeO_2, and oxygen.

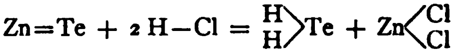


$$2\,\mathrm{Te}\begin{array}{l}/\!\!/\mathrm{O}\\ =\mathrm{O}\\ \backslash\!\!\backslash\mathrm{O}\end{array} = 2\,\mathrm{Te}\begin{array}{l}/\!\!/\mathrm{O}\\ \backslash\!\!\backslash\mathrm{O}\end{array} + \mathrm{O{=}O}$$

Tellurium combines with metals to form *tellurides*. Thus, by fusing together tellurium and zinc, *zinc telluride*, ZnTe, may be formed.

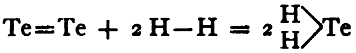
$$2\,\mathrm{Zn} + 2\,\mathrm{Te} = 2\,\mathrm{ZnTe}$$

By acting upon zinc telluride, ZnTe, with hydrochloric acid, or other similar acid, *hydrogen telluride*, H_2Te, may be evolved as a colorless, strong-smelling, poisonous gas,



$$\mathrm{Zn{=}Te} + 2\,\mathrm{H{-}Cl} = \begin{array}{l}\mathrm{H}\diagdown\\ \mathrm{H}\diagup\end{array}\!\!\mathrm{Te} + \mathrm{Zn}\begin{array}{l}\diagup\mathrm{Cl}\\ \diagdown\mathrm{Cl}\end{array}$$

and the same compound may be made in small quantities by sufficiently heating tellurium with hydrogen.



$$\mathrm{Te{=}Te} + 2\,\mathrm{H{-}H} = 2\begin{array}{l}\mathrm{H}\diagdown\\ \mathrm{H}\diagup\end{array}\!\!\mathrm{Te}$$

Hydrogen telluride is a colorless, poisonous gas of strong odor, burning with a blue flame, soluble in water with formation of a solution from which tellurium separates upon exposure to the air. By acting upon solutions of compounds of metals with hydrogen telluride solution, *tellurides* may be formed, some of which are insoluble. Solutions of tellurides separate tellurium spontaneously on standing exposed to the air.

Tellurium dichloride, $TeCl_2$, and *tellurium tetrachloride*, $TeCl_4$, are crystalline substances formed by direct combination of chlorine with tellurium, easily melted and vaporized, and decomposed by water, with formation of tellurous acid. Similar bromides and iodides of tellurium are known.

By the action of tellurium upon sulphur trioxide, *tellurium sulphur trioxide*, $TeSO_3$, may be formed as a red, amorphous, transparent solid, which melts at 30°; is decomposed by water with formation of tellurium and other products, and may be decomposed by heating, with formation of sulphur dioxide and *tellurium monoxide*, TeO, a brownish black, amorphous solid. By acting upon tellurium monoxide with sulphuric acid, a red solution is obtained, from which crystals of *tellurium sulphate*, $Te(SO_4)_2$, separate, while the compound $TeSO_3$ remains in solution.

alkali earth elements are found dissolved in sea water and certain mineral waters, and also occur in solid deposits, such as are found in Stassfurt in Germany, and in New York and Michigan, the element fluorine being found only in small amounts in soluble fluorides. Fluorine compounds are present in the enamel of teeth and in traces in bones and other animal tissues. The principal minerals containing fluorine are *fluorite* (*fluorspar*), CaF_2; *apatite*, a double fluoride and phosphate of calcium, sometimes having the composition $Ca_4(CaF)(PO_4$ and *cryolite*, $3\,NaF \cdot AlF_3$, a double fluoride of sodium and aluminium. From the mineral fluorides fluorine may be artificially prepared.

Chlorine. Chlorine, the most important of the halogens, is found as a constituent of various soluble chlorides, the most abundant of which are sodium chloride, NaCl, potassium chloride, KCl, and magnesium chloride, $MgCl_2$. Sodium chloride, NaCl, the ordinary *sea salt*, is found in large amounts in solution in sea water, of which it forms between two and three per cent. part by weight, and in many mineral waters, while as *halite* (*rock salt*) it is the chief constituent of the deeper portion of the deposit at Stassfurt, and is found in large deposits in many other places. Potassium chloride and magnesium chloride are found associated with sodium chloride in solution in smaller amounts. At Stassfurt and elsewhere potassium chloride is found alone as the mineral *sylvite*, and associated with the more important mineral *carnallite*, $KCl \cdot MgCl_2 \cdot 6\,H_2O$. The bodies of plants and animals contain sodium chloride, a small amount of which is a necessary ingredient of animal food.

Brines. When the concentrated *brines*, obtained from sea water or mineral water, or by dissolving the solid salt deposits in water, are allowed to evaporate, the less soluble sodium chloride crystallizes out first, leaving a concentrated "mother liquor," or *bittern*, which holds in solution salts of other halogen elements. The chlorine of commerce is obtained by decomposing sodium chloride by suitable agents. We have already seen how sodium chloride is utilized as "table salt," and as a source of other sodium compounds.

Bromine and Iodine. Bromine and iodine are found combined with alkali elements and alkali earth elements in soluble bromides and iodides, which are associated with the chlorides in small amounts in sea water and mineral waters, while bromides are also found associated with a solid which melts at −92.5°. Hydrogen fluoride gas fumes strongly in moist air, and in the presence of moisture is extremely corrosive, attacking all metals except lead, gold, and platinum, all oxides, including the refractory silicon dioxide, and many salts, including the silicates.

Hydrogen fluoride is extremely soluble in water, forming a strongly fuming colorless solution, from which the gas may be evolved by heating. The saturated solution of hydrogen fluoride boils at 120°, forming a vapor which may be condensed to a liquid of specific gravity 1.15, containing 35.3 per cent. of hydrogen fluoride. Hydrogen fluoride is classed with the monobasic acids, since it contains a positive hydrogen-ion, replaceable by positive elements, with formation of salts. Its solution in water is generally called *hydrofluoric acid.* Since hydrofluoric acid is extremely volatile and active chemically, attacking glass readily, it is best preserved in solution in bottles of paraffin or platinum kept in a cool place. Hydrofluoric acid has an exceedingly caustic action upon the skin, causing deep burns which heal with difficulty, and it acts as a poison when its fumes are inhaled.

The specific gravity of hydrogen fluoride gas at 100° is 20.01, corresponding to a molecular weight indicated by the symbol HF. As the temperature is lowered, the pressure being approximately the same, its specific gravity increases, which would show that at lower temperature the molecules of hydrogen fluoride are more complex than the symbol HF would indicate. At 30° the molecular condition corresponds to the symbol H_2F_2, or $H-F=F-H$.

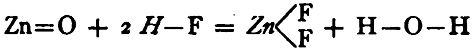
Soluble Fluorides. *The fluorides may be formed by acting with hydrofluoric acid upon basic hydroxides and oxides, salts of volatile acids, and positive elements.* Thus, *sodium fluoride*, NaF, is formed by acting with hydrofluoric acid, HF, upon sodium hydroxide, sodium carbonate, or sodium, with the formation at the same time of water, or of water and carbon dioxide, or hydrogen, respectively.

$$Na-O-H + H-F = Na-F + H-O-H$$

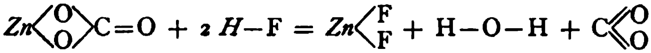
$$\left.\begin{matrix}Na-O\\Na-O\end{matrix}\right\rangle C = O + 2\,H-F = 2\,Na-F + H-O-H + C\left\langle\begin{matrix}O\\O\end{matrix}\right.$$

$$2\,Na + 2\,H-F = 2\,Na-F + H-H$$

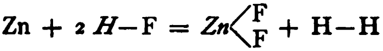
In like manner *zinc fluoride*, ZnF_2, is obtained by acting upon zinc oxide, ZnO, zinc carbonate, $ZnCO_3$, or zinc, with hydrofluoric acid.



$$\mathrm{Zn{=}O} + 2\,H\mathrm{-F} = Zn{<}\genfrac{}{}{0pt}{}{\mathrm{F}}{\mathrm{F}} + \mathrm{H{-}O{-}H}$$



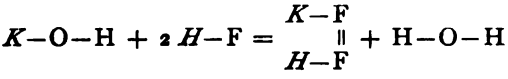
$$Zn{<}\genfrac{}{}{0pt}{}{\mathrm{O}}{\mathrm{O}}{>}\mathrm{C{=}O} + 2\,H\mathrm{-F} = Zn{<}\genfrac{}{}{0pt}{}{\mathrm{F}}{\mathrm{F}} + \mathrm{H{-}O{-}H} + \mathrm{C}{\lll}\genfrac{}{}{0pt}{}{\mathrm{O}}{\mathrm{O}}$$



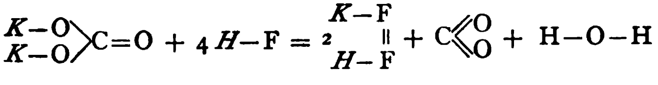
$$\mathrm{Zn} + 2\,H\mathrm{-F} = Zn{<}\genfrac{}{}{0pt}{}{\mathrm{F}}{\mathrm{F}} + \mathrm{H{-}H}$$

The fluorides of many other positive elements, such as *calcium fluoride*, CaF_2, and *aluminium fluoride*, AlF_3, are known, as well as fluorides of some negative elements, such as *boron fluoride*, BF_3, and *silicon fluoride*, SiF_4.

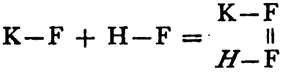
In the simple fluorides, like boron trifluoride, BF_3, and silicon tetrafluoride, SiF_4, of which the molecular weights and molecular symbols may be found from the specific gravities of the gaseous substances, fluorine exhibits a valence of I. These simple fluorides may be considered to be derived from hydrofluoric acid, of the constitution H — F, which exists at 100°, by the complete replacement of hydrogen by other elements. There are, however, more complex fluorides which correspond to a hydrofluoric acid, of the constitution H_2F_2, which exists at 30°. Thus, although neutral fluorides of the ordinary type may be formed by the complete replacement of the hydrogen of hydrofluoric acid by positive elements, when the hydrogen is only partially replaced, acidic fluorides containing hydrogen may be formed, and the same compounds may be obtained by the direct combination of neutral fluorides with hydrofluoric acid. Thus, by the action of an excess of hydrofluoric acid upon potassium hydroxide, or potassium carbonate, or by the combination of hydrofluoric acid with potassium fluoride, the acidic *potassium hydrogen fluoride*, KHF_2, may be formed.



$$K\mathrm{-O-H} + 2\,H\mathrm{-F} = \begin{array}{c}K\mathrm{-F}\\ \Vert\\ H\mathrm{-F}\end{array} + \mathrm{H{-}O{-}H}$$



$$\begin{array}{l}K\mathrm{-O}\\ K\mathrm{-O}\end{array}{>}\mathrm{C{=}O} + 4\,H\mathrm{-F} = 2\begin{array}{c}K\mathrm{-F}\\ \Vert\\ H\mathrm{-F}\end{array} + \mathrm{C}{\lll}\genfrac{}{}{0pt}{}{\mathrm{O}}{\mathrm{O}} + \mathrm{H{-}O{-}H}$$



$$\mathrm{K{-}F} + \mathrm{H{-}F} = \begin{array}{c}\mathrm{K{-}F}\\ \Vert\\ H\mathrm{-F}\end{array}$$

Boron fluoride, BF_3, combines with hydrofluoric acid, HF, to form *hydrogen borofluoride*, HBF_4 (hydrofluoboric acid), which acts upon bases and other suitable compounds to form salts known as *fluoborates*, such as *sodium fluoborate*, $NaBF_4$. Similarly, silicon fluoride, SiF_4, combines with hydrofluoric acid to form *hydrogen silicofluoride*, H_2SiF_6 (hydrofluosilicic acid), which forms salts known as *fluosilicates*.

been intimated in our study of the compounds of boron and silicon, they may also be considered to be derived from boric acid and silicic acid respectively, by substitution of fluorine for oxygen. Many double fluorides of two or more elements, such as $AsF_5 \cdot KF$, and $AsF_5 \cdot 2\,KF$, are known, and the similar *cryolite*, $3\,NaF \cdot AlF_3$, is found as a mineral.

Insoluble Fluorides. *The fluorides of the alkali earth elements are insoluble and may be formed as precipitates.* When a soluble calcium compound, such as calcium chloride, is added to a water solution of a fluoride like sodium fluoride, NaF, white *calcium fluoride*, CaF_2, is precipitated,

$$2\,NaF + CaCl_2 = \mathbf{CaF_2} + 2\,NaCl$$

and by acting upon a solution of sodium fluoride with soluble barium chloride, white *barium fluoride*, BaF_2, is precipitated.

$$2\,NaF + BaCl_2 = \mathbf{BaF_2} + 2\,NaCl$$

Strong acids act upon these insoluble fluorides.

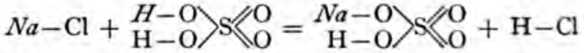
Etching of Glass by Hydrofluoric Acid. *The action of hydrofluoric acid upon silicates to form gaseous silicon fluoride, which acts upon water to form silicic acid, may be utilized to identify hydrofluoric acid and fluorides.* Although anhydrous hydrogen fluoride is without action upon glass, ordinary hydrofluoric acid attacks glass, etching its surface and rendering it opaque. When a substance containing a fluoride in finely divided condition is moistened with concentrated sulphuric acid and very gently warmed, hydrofluoric acid is evolved and will attack any exposed surface of glass. If now a watch glass previously covered with a layer of paraffin, and marked with a design cut through the paraffin, is placed upon the dish and allowed to remain for a suitable time, the design will be found, after removing the paraffin, to have been permanently etched into the glass.

If to a substance containing a fluoride, sulphuric acid and a small quantity of powdered glass or some other silicate are added and the mixture warmed, gaseous silicon fluoride is evolved, which on striking a moistened glass rod held over the opening of the vessel deposits on the rod a coating of gelatinous silicic acid.

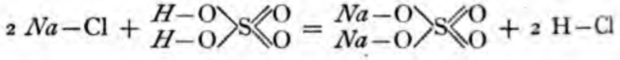
Electrolysis of Hydrogen Fluoride. *By the electrolysis of pure anhydrous hydrogen fluoride, under proper conditions, fluorine may be liberated.* Fluorine may be obtained in quantity by passing a strong electric current through a mixture of 5 parts of anhydrous hydrogen fluoride, and 1 part of potassium hydrogen fluoride contained in a U-tube of iridium-plati-

In our study of chlorine compounds we start most naturally with the sodium chloride, NaCl, or common salt, which occurs throughout the sea waters and in salt deposits.

Hydrogen Chloride. When sodium chloride, NaCl, and sulphuric acid act upon one another, either sodium hydrogen sulphate, or sodium sulphate, is produced, according to the proportions of the reagents used, while gaseous *hydrogen chloride*, HCl, is evolved.



$$\mathit{Na}{-}\mathrm{Cl} + \begin{matrix}\mathit{H}{-}\mathrm{O}\\ \mathrm{H}{-}\mathrm{O}\end{matrix}\!\!>\!\mathrm{S}\!<\!\!\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix} = \begin{matrix}\mathit{Na}{-}\mathrm{O}\\ \mathrm{H}{-}\mathrm{O}\end{matrix}\!\!>\!\mathrm{S}\!<\!\!\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix} + \mathrm{H}{-}\mathrm{Cl}$$



$$2\,\mathit{Na}{-}\mathrm{Cl} + \begin{matrix}\mathit{H}{-}\mathrm{O}\\ \mathit{H}{-}\mathrm{O}\end{matrix}\!\!>\!\mathrm{S}\!<\!\!\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix} = \begin{matrix}\mathit{Na}{-}\mathrm{O}\\ \mathit{Na}{-}\mathrm{O}\end{matrix}\!\!>\!\mathrm{S}\!<\!\!\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix} + 2\,\mathrm{H}{-}\mathrm{Cl}$$

To prepare pure hydrogen chloride in quantity we may pour over 5 parts of sodium chloride, contained in an ordinary generating flask, 9 parts of sulphuric acid previously diluted with 2 parts of water, and warm the flask gently. The hydrogen chloride, evolved in a steady stream, is passed through a washing flask containing sulphuric acid, to free it from water, and collected over mercury in a pneumatic trough. Hydrogen chloride may also be obtained by the combination of chlorine with hydrogen, and is a product of the action of chlorine and of certain chlorides upon water, of the action of chlorine upon hydrocarbons, and of other reactions.

Hydrogen chloride, HCl, is a colorless gas of specific gravity 36.46, possessing a pungent odor and acid taste. The observed specific gravity of the gas, corresponding to the molecular symbol HCl, remains constant for all ordinary temperatures, but becomes less above 1400°, indicating that at this high temperature some dissociation of the molecule into hydrogen and chlorine atoms has set in. By cold and pressure, hydrogen chloride may be condensed to a colorless liquid of specific gravity 0.83 at 15°; it freezes at −115.7° to white crystals which melt at −112.5°; and it boils at −80.3° under ordinary pressure.

When exposed to moist air gaseous hydrogen chloride unites with particles of water to form a white mist. Gaseous hydrogen chloride is readily soluble in water, forming a colorless solution which when concentrated fumes strongly. Hydrogen chloride is a monobasic acid, con-

Chlorides of Positive Elements. In like manner chlorides of nearly all the more positive elements, including the alkali elements and alkali earth elements and the heavier metals, may be made by the action of hydrochloric acid upon the elements themselves or their oxides, hydroxides, or suitable salts.

Insoluble Chlorides. *From soluble chlorides, the chlorides of silver, mercury in its condition of lower valence, and lead may be formed as insoluble precipitates.*

When to a soluble silver compound such as silver nitrate, $AgNO_3$, is added a solution of hydrochloric acid, or of a soluble chloride such as sodium chloride, NaCl, a curdy white precipitate of *silver chloride*, AgCl, readily acted upon by ammonium hydroxide, and turning dark under influence of light, is obtained.

$$AgNO_3 + HCl = \mathbf{AgCl} + HNO_3$$

When to a soluble mercurous compound such as mercurous nitrate, $Hg_2(NO_3)_2$, is added a solution of hydrochloric acid or sodium chloride, a white pulverulent precipitate of *mercurous chloride*, Hg_2Cl_2, forms.

$$Hg_2(NO_3)_2 + 2\ HCl = \mathbf{Hg_2Cl_2} + 2\ HNO_3$$

When to lead acetate, $Pb(C_2H_3O_2)_2$, or some other soluble lead salt, hydrochloric acid or a solution of sodium chloride is added, a white flocculent precipitate of *lead chloride*, $PbCl_2$, acted upon by strong hydrochloride acid, and moderately soluble in hot water, is formed.

$$Pb(C_2H_3O_2)_2 + 2\ HCl = \mathbf{PbCl_2} + 2\ H(C_2H_3O_2)$$

Chlorides of Negative Elements. The chlorides of many negative elements, such as phosphorus and sulphur, not usually obtainable by the action of hydrochloric acid upon the elements, oxides or hydroxides, may be made by the action of chlorine upon the elements.

Electrolysis of Hydrochloric Acid. *Hydrochloric acid may be decomposed by the electric current with the evolution of hydrogen and chlorine.* Hydrogen chloride is an extremely stable substance, and only at extremely high temperatures does it show a tendency to dissociate into hydrogen and chlorine. When, however, an electric current of moderate intensity is passed through a concentrated solution of hydrochloric acid, greenish yellow chlorine gas will be evolved at the positive pole, and hydrogen will be liberated at the negative pole.

By acting upon the manganous chloride solution with calcium hydroxide, calcium chloride and manganous hydroxide may be formed, and if at the same time a stream of air is sent through the mixture, the manganous hydroxide may be oxidized with formation of manganese compounds, which may be used to liberate chlorine from more hydrochloric acid. The *Weldon process* for the manufacture of chlorine is based upon these reactions, which make it possible to set free one half the total amount of chlorine in hydrochloric acid by the oxidizing action of manganese compounds, which may be formed and used again.

When manganese dioxide, MnO_2, acts upon hydrochloric acid in the presence of sulphuric acid, manganous sulphate, $MnSO_4$, is formed in solution, all of the chlorine of the hydrochloric acid being evolved.

$$2\,HCl + MnO_2 + H_2SO_4 = MnSO_4 + 2\,H_2O + Cl_2$$

To prepare chlorine for laboratory purposes by the process, hydrochloric acid is formed by the action of a suitable excess of sulphuric acid upon sodium chloride and manganese dioxide, sodium sulphate and manganous sulphate being formed in solution, all of the chlorine being set free.

$$2\,NaCl + MnO_2 + 3\,H_2SO_4 = 2\,NaHSO_4 + MnSO_4 + 2\,H_2O + Cl_2$$

In an ordinary generating flask a mixture is made of 5 parts of manganese dioxide with 11 parts of sodium chloride, and through a thistle tube are added 14 parts of sulphuric acid mixed with 7.5 parts of water. As the mixture is gently warmed the chlorine is evolved in a steady stream, and may be collected over warm water. Still other oxygen compounds, such as the chloric acid and chromic acid and dichromic acid and their salts, may be employed to oxidize hydrochloric acid with evolution of chlorine.

Chlorine may also be obtained by decomposing suitable chlorides by electricity or by heating, and by oxidizing some chlorides by means of oxygen or oxygen compounds.

Chlorine. *Chlorine*, first prepared by Scheele in 1774, by acting upon hydrochloric acid with maganese dioxide, and recognized as an element by Gay-Lussac and Thenard in 1809, and by Davy in 1810, is a yellowish green gas of specific gravity 70.52, possessing a characteristic suffocating odor. Under 1 atmosphere pressure at $-40°$, or under 57 atmospheres at 15°, it forms a yellow liquid, of specific gravity 1.55 at $-33.6°$, at which temperature it boils. At a very low temperature chlorine may form a yellow crystalline solid which melts at $-102°$. Chlorine is sparingly soluble in water, 1 volume of water at 20° holding 2 volumes of chlorine, and at 10° holding 2.5 volumes. The water solumediate chlorine compounds containing oxygen may be formed. This decomposition of water by chlorine is the reversal of the reaction by which chlorine and water are formed in the reaction between oxygen and hydrogen chloride, and must be represented as a reversible reaction.

$$2\,H_2O + 2\,Cl_2 \rightleftarrows 4\,HCl + O_2$$

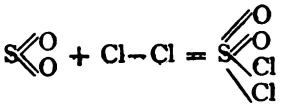
Chlorine as a Bleaching Agent. The action of chlorine in liberating oxygen from water explains its use as an indirect oxidizing agent in the presence of moisture. Thus, vegetable coloring matters, such as those found in the leaves of flowers and in artificial dyes, are all *bleached* by chlorine in the presence of moisture, although dry chlorine fails to act upon them. In the same manner the impurities in ordinary air, such as the particles which cause bad odors and the vegetable organisms which spread disease, are destroyed by moist chlorine, which is therefore a valuable *disinfectant* and *antiseptic.* It is probable that the bleaching of most coloring matters as well as the destruction of organic particles and organisms is due to the action of the oxygen, which, at the moment of its liberation by chlorine, is far more active than ordinary oxygen. Large quantities of chlorine, and of compounds which readily evolve chlorine, are used for bleaching cloth fabrics, as well as for disinfecting and sterilizing. The use of chlorine as a bleacher requires the subsequent application of a suitable substance, such as sodium thiosulphate, as an *antichlor* to remove from the fabric the excess of chlorine and the hydrochloric acid formed.

Chlorine and Hydrocarbons. Chlorine acts upon gaseous hydrocarbons spontaneously, and often with explosive violence. In the action of chlorine upon methane, CH_4, four products, *methyl chloride*, CH_3Cl, *methylene chloride*, $C_2H_2Cl_2$, *chloroform*, $CHCl_3$, and *carbon tetrachloride*, CCl_4, are obtained. Of these the first is a gas and the others are colorless liquids of low boiling points.

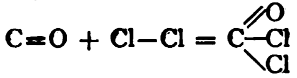
$$\begin{aligned}
CH_4 + Cl_2 &= CH_3Cl + HCl\\
CH_4 + 2\,Cl_2 &= CH_2Cl_2 + 2\,HCl\\
CH_4 + 3\,Cl_2 &= CHCl_3 + 3\,HCl\\
CH_4 + 4\,Cl_2 &= CCl_4 + 4\,HCl
\end{aligned}$$

Chloroform is of importance as an anæsthetic. Chlorine derivatives of many other hydrocarbons may be made in similar manner, and when the hydrocarbon is rich in carbon some of this element may be set free. Thus, a piece of paper wet in turpentine, $C_{10}H_{16}$, when thrust into a jar of dry chlorine, bursts into flame and evolves clouds of finely divided carbon.

Sulphuryl chloride, SO_2Cl_2, may be made by direct combination of chlorine with sulphur dioxide, SO_2.



Carbonyl chloride, $COCl_2$, may be formed by combination of chlorine and carbon monoxide, CO.



Chloranhydrides. Compounds of chlorine with oxides of the more negative elements, such as nitroxyl chloride, NO_2Cl, nitrosyl chloride, NOCl, sulphuryl chloride, SO_2Cl_2, and carbonyl chloride, $COCl_2$, are called *chloranhydrides*, because they may be hydrolyzed with formation of hydrochloric acid and an acid formed by the replacement of the chlorine of the chloranhydride by the hydroxyl group.

$$\begin{aligned} NO_2Cl + H_2O &= HCl + HNO_3 \\ SO_2Cl_2 + 2\,H_2O &= 2\,HCl + H_2SO_4 \\ COCl_2 + 2\,H_2O &= 2\,HCl + H_2CO_3 \\ &= 2\,HCl + H_2O + CO_2 \end{aligned}$$

Chlorine and Oxides with Carbon. *Certain oxides with which chlorine will not combine may be attacked by chlorine in presence of a suitable reducing agent.* Thus, when chlorine is passed over aluminium oxide, Al_2O_3, heated to redness in the presence of finely divided carbon, aluminium chloride, $AlCl_3$, and carbon monoxide, CO, are formed simultaneously.

$$Al_2O_3 + 3\,C + 3\,Cl_2 = 2\,AlCl_3 + 3\,CO$$

Similarly, boron trichloride, BCl_3, is obtained by passing chlorine into a heated mixture of boron trioxide, B_2O_3, and carbon; and silicon chloride, $SiCl_4$, may be formed by the action of chlorine upon a mixture of silicon dioxide, SiO_2, and carbon. Taken alone, chlorine is unable to form chlorides from any one of these oxides, and no one of them is reducible by carbon acting alone.

Electrolysis of Chlorides. *Like hydrochloric acid, the soluble chlorides of the positive elements may be decomposed by electrolysis with evolution of chlorine.* When an electrical current of suitable strength is passed and ferric chloride, $FeCl_3$, may be similarly broken down into ferrous chloride, $FeCl_2$, chlorine being evolved.

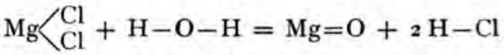
$$2\,FeCl_3 = 2\,FeCl_2 + Cl_2$$

Auric chloride, $AuCl_3$, evolves chlorine when heated, forming first aurous chloride, AuCl, which finally decomposes, leaving a residue of gold.

$$AuCl_3 = AuCl + Cl_2$$

$$2\,AuCl = 2\,Au + Cl_2$$

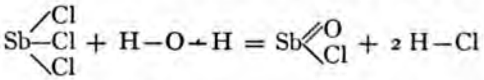
Hydrolysis of Chlorides. *Many chlorides are decomposed by water with the formation of hydrogen chloride and oxides, oxychlorides, or hydroxides of their characteristic elements.* When a water solution of magnesium chloride, $MgCl_2$, is evaporated to dryness at low temperature, the magnesium chloride separates out in crystalline form, with the composition $MgCl_2 \cdot 6\,H_2O$. When, however, crystallized magnesium chloride is heated to high temperature, it is hydrolyzed with formation of some magnesium oxide, and evolution of hydrogen chloride.



$$\mathrm{Mg}\begin{matrix}\diagup\mathrm{Cl}\\ \diagdown\mathrm{Cl}\end{matrix} + \mathrm{H-O-H} = \mathrm{Mg{=}O} + 2\,\mathrm{H-Cl}$$

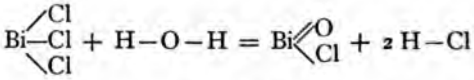
In similar manner calcium chloride, $CaCl_2$, aluminium chloride, $AlCl_3$, ferric chloride, $FeCl_3$ and many other chlorides may be acted upon by water at high temperature.

When antimony trichloride, $SbCl_3$, is put into an excess of cold water, an *antimony oxychloride* of more or less complex composition, the simplest form of which has the composition SbOCl, may be formed.



$$\mathrm{Sb}\begin{matrix}\diagup\mathrm{Cl}\\ -\mathrm{Cl}\\ \diagdown\mathrm{Cl}\end{matrix} + \mathrm{H-O-H} = \mathrm{Sb}\begin{matrix}\diagup\!\!\diagup\mathrm{O}\\ \diagdown\mathrm{Cl}\end{matrix} + 2\,\mathrm{H-Cl}$$

and in similar manner by the action upon bismuth trichloride, $BiCl_3$, of an excess of water, *bismuth oxychloride*, BiOCl, is formed.



$$\mathrm{Bi}\begin{matrix}\diagup\mathrm{Cl}\\ -\mathrm{Cl}\\ \diagdown\mathrm{Cl}\end{matrix} + \mathrm{H-O-H} = \mathrm{Bi}\begin{matrix}\diagup\!\!\diagup\mathrm{O}\\ \diagdown\mathrm{Cl}\end{matrix} + 2\,\mathrm{H-Cl}$$

When phosphorus pentachloride, PCl_5, acts upon a small amount of water, phosphorus oxychloride, $POCl_3$, and hydrogen chloride are formed.

all of which are found native. Another important mineral chloride is *carnallite*, $KCl \cdot MgCl_2 \cdot 6\ H_2O$, and other complex minerals, such as *matlockite*, $PbCl_2 \cdot PbO$, and *atacamite*, $Cu_2Cl(OH)_3$, occur in small quantities. We have also studied the chlorides of boron, aluminium, carbon, silicon, nitrogen, phosphorus, and sulphur, which decompose water often spontaneously, and take part in many chemical changes. We have still to study the chlorides of copper, silver, gold, zinc, lead, tin, iron, and of some other elements. Sodium chloride is used as a food and as a source for sodium carbonate and chlorine compounds; potassium chloride is used as a fertilizer and as a source for potassium nitrate and other potassium compounds; some of the chlorides of negative elements are useful reagents.

Double Chlorides. *The chlorides of certain positive elements combine readily with one another to form double chlorides.* By bringing different chlorides together in solution in proper proportions and evaporating the mixtures, many double chlorides may be formed, some of which are anhydrous, while others contain water of crystallization. We have already noted the double chloride $NaCl \cdot AlCl_3$. The double chloride found in the mineral *carnallite*, $KCl \cdot MgCl_2 \cdot 6\ H_2O$, and the sodium compound, $NaCl \cdot MgCl_2 \cdot H_2O$, may be made artificially. Among the many double chlorides of the alkali elements with metals are $KCl \cdot AgCl$, $KCl \cdot AuCl$, $KCl \cdot PtCl_2$, and $2\ KCl \cdot PtCl_4$.

Oxides and Hydroxides. Although chlorine does not combine with oxygen directly, three chlorine oxides may be formed indirectly, while three acidic chlorine hydroxides are known. All the compounds containing chlorine and oxygen may be readily decomposed.

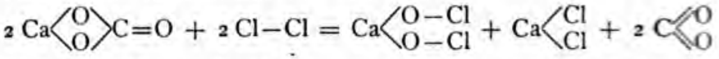
OXIDES	HYDROXIDES
Chlorine monoxide, Cl_2O	Hypochlorous acid, $HClO$ *
Chlorine dioxide, ClO_2	[Chlorous acid, $HClO_2$] †
	Chloric acid, $HClO_3$
Chlorine heptoxide, Cl_2O_7	Perchloric acid, $HClO_4$

* Known in solution.

† Represented by salts.

The hypochlorites and chlorates may be readily formed by acting upon basic hydroxides or carbonates of positive elements with chlorine, and

Similarly, chlorine will act upon an excess of calcium carbonate, held in suspension in water, with formation of mixed *calcium hypochlorite*, $Ca(ClO)_2$, and *calcium chloride.*



$$2\,\mathrm{Ca}\langle{}^{\mathrm{O}}_{\mathrm{O}}\rangle\mathrm{C{=}O} + 2\,\mathrm{Cl{-}Cl} = \mathrm{Ca}\langle{}^{\mathrm{O-Cl}}_{\mathrm{O-Cl}} + \mathrm{Ca}\langle{}^{\mathrm{Cl}}_{\mathrm{Cl}} + 2\,\mathrm{C}\langle\!\langle{}^{\mathrm{O}}_{\mathrm{O}}$$

Other hypochlorites besides those mentioned may be made by action of chlorine upon hydroxides or carbonates in solution, but because of their instability they are with difficulty separated from the chlorides formed at the same time. A nearly pure solution of a hypochlorite may be obtained, however, by neutralizing a solution of hypochlorous acid, HClO, with a basic hydroxide.

Instability of Hypochlorites. Because of their instability, however, the *hypochlorites* cannot be prepared in pure condition, and are known only in solution; and, even in solution, the hypochlorites tend to decompose upon heating with the formation of chlorides and chlorates.

When chlorine acts upon the solution of a hypochlorite, some hypochlorous acid is formed, which by its action upon the remaining hypochlorite produces further decomposition with formation of a chlorate and hydrochloric acid. This is why it is best, in making hypochlorites, to act in the cold with a regulated amount of chlorine upon an excess of the basic hydroxide or the carbonate.

Bleaching Compounds. Because of the readiness with which they evolve oxygen and chlorine, the hypochlorites are strong oxidizers and find a wide use for *bleaching* and *disinfecting* purposes, being much more convenient for handling and application than chlorine. The solution of potassium hypochlorite and potassium chloride, made by absorbing chlorine in potassium carbonate, is a commercial product known as *eau de Javelles.* The product formed when chlorine acts upon dry calcium hydroxide or calcium oxide, a compound of the composition $CaCl(ClO)$ is known as "chloride of lime," or *bleaching powder.* In use these bleaching and disinfecting compounds are best decomposed by dilute acids with the formation of hypochlorous acid or chlorine, which cause the indirect oxidization of the coloring matters or infectious matters to which they are applied. When a weak acid is employed, for example carbonic acid derived from the carbon dioxide of the air, or when a stronger acid is used in regulated amount, only the hypochlorite of the mixture is attacked and hypochlorous acid alone is formed; but a sufficient amount of a strong acid forms hydrochloric acid likewise, which reacts with the hypochlorous acid to evolve chlorine. Thus, the action of sulphuric acid upon chloride of lime, corresponding in composition to a mixture of calcium hypochlorite, $Ca(ClO)_2$, and calcium chloride, $CaCl_2$, gives calcium sulphate, water, and chlorine.

and by passing chlorine into solutions of salts of stronger acids, such as sodium sulphate, hypochlorous acid and sodium chloride are formed.

$$Cl_2 + Na_2SO_4 + H_2O = HClO + NaCl + NaHSO_4$$

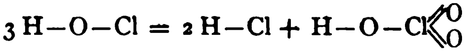
When the dilute solution of hypochlorous acid, containing chlorides or other salts, is distilled, the *hypochlorous acid*, HClO, passes over in the distillate and condenses in a water solution, which is colorless when dilute and orange-yellow when concentrated, and which possesses a characteristic odor like that of chlorine. When concentrated solutions containing hypochlorous acid are distilled, some of the acid may decompose with liberation of chlorine, but this may be expelled by blowing a current of air through the solution.

Decomposition of Hypochlorous Acid.

Hypochlorous acid decomposes under the action of light or heat into hydrochloric acid and oxygen, or into hydrochloric acid and chloric acid, or chlorine and water, according to the conditions. When a solution of hypochlorous acid, HClO, is allowed to stand exposed to light or is warmed, oxygen is slowly evolved, and hydrochloric acid is formed in solution.

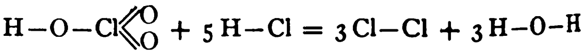
$$2\,H{-}O{-}Cl = 2\,H{-}Cl + O{=}O$$

At the same time some chloric acid, $HClO_3$, may be formed by the decomposition of the hypochlorous acid in proper proportions,



$$3\,H{-}O{-}Cl = 2\,H{-}Cl + H{-}O{-}Cl\begin{smallmatrix}\nearrow\!\!\!\nearrow O\\ \searrow\!\!\!\searrow O\end{smallmatrix}$$

and by the reaction of the chloric acid, $HClO_3$, with the hydrochloric acid, chlorine may be evolved and water formed.



$$H{-}O{-}Cl\begin{smallmatrix}\nearrow\!\!\!\nearrow O\\ \searrow\!\!\!\searrow O\end{smallmatrix} + 5\,H{-}Cl = 3\,Cl{-}Cl + 3\,H{-}O{-}H$$

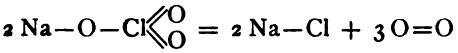
At the same time the hypochlorous acid may react directly with the hydrochloric acid to form water and liberate chlorine.

$$2\,H{-}O{-}Cl + 2\,H{-}Cl = 2\,Cl{-}Cl + 2\,H{-}O{-}H$$

Dilute solutions of hypochlorous acid decompose only slightly when allowed to stand in the light or when warmed, but when the solutions are concentrated, the decomposition will proceed to an extent dependent upon conditions of concentration and temperature.

Other hydroxides and carbonates may be similarly acted upon by chlorine. *Potassium chlorate*, $KClO_3$, is made commercially by passing chlorine in excess into milk of lime and adding an equivalent amount of potassium chloride. It forms tabular crystals which melt at 359° and begin to decompose at 372°. It is used in medicine, and in the manufacture of matches and of fireworks. The more soluble *sodium chlorate*, $NaClO_3$, is made by adding sodium sulphate to a solution of calcium chlorate made by saturating milk of lime with chlorine. The chlorates are also made by the electrolysis of solutions of the corresponding chlorides in presence of an alkali hydroxide or under conditions which permit the chlorine evolved at the anode to act upon the basic hydroxide formed at the cathode at a temperature sufficient to decompose the hypochlorite first formed.

Dissociation of Chlorates. *When chlorates are sufficiently heated, oxygen is evolved.* When sodium chlorate, $NaClO_3$, is sufficiently heated, oxygen is evolved, and sodium chloride, NaCl, remains as residue.



$$2\,Na{-}O{-}Cl\begin{matrix}\diagup\!\!\diagup O\\ \diagdown\!\!\diagdown O\end{matrix} = 2\,Na{-}Cl + 3\,O{=}O$$

If the heat of the reaction be moderated, sodium perchlorate, $NaClO_4$, may be formed as an intermediate product. This action will be discussed presently.

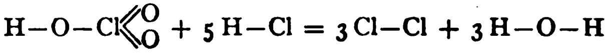
Potassium chlorate, $KClO_3$, and other chlorates, may be similarly decomposed by sufficient heating. Oxygen is usually prepared for laboratory purposes by heating potassium chlorate. The presence of certain oxides of metals, such as manganese dioxide, MnO_2, ferric oxide, Fe_2O_3, cupric oxide, CuO, facilitates the decomposition of chlorates by heat, by mechanically preventing the fusion of the mass, and also by catalytic action.

The chlorates are strong oxidizers, and dry mixtures containing chlorates and sulphur, phosphorus, or combustible carbon compounds will detonate violently when heated or when sharply struck.

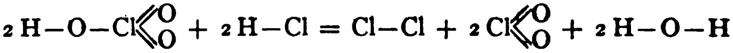
Chloric Acid. *Chloric acid may be formed from chlorates by the action of suitable reagents in solution.*

Dilute sulphuric acid acts upon chlorates in solution to form chloric acid. Thus, when dilute sulphuric acid acts upon potassium

By the action of hydrochloric acid upon chloric acid, chlorine and water are formed, with some admixture of chlorine dioxide, depending upon conditions of dilution and temperature.



$$\mathrm{H-O-Cl}\begin{matrix}\scriptstyle =O\\ \scriptstyle =O\end{matrix} + 5\,\mathrm{H-Cl} = 3\,\mathrm{Cl-Cl} + 3\,\mathrm{H-O-H}$$

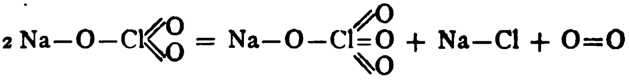


$$2\,\mathrm{H-O-Cl}\begin{matrix}\scriptstyle =O\\ \scriptstyle =O\end{matrix} + 2\,\mathrm{H-Cl} = \mathrm{Cl-Cl} + 2\,\mathrm{Cl}\begin{matrix}\scriptstyle =O\\ \scriptstyle =O\end{matrix} + 2\,\mathrm{H-O-H}$$

The addition of hydrochloric acid to a chlorate, or of sulphuric acid to a mixture of a chlorate and a chloride, such as may be obtained in solution by the action of chlorine upon basic hydroxides or carbonates of positive elements, results in the formation of a chloride or sulphate respectively, and the liberation of chlorine.

Chloric acid is a strong oxidizer, and its concentrated water solution will cause sulphur, phosphorus, alcohol, and paper and other combustible substances to inflame spontaneously when brought into contact with it. It neutralizes bases, with the formation of corresponding chlorates and water.

Perchlorates. *Perchlorates may be formed, together with the corresponding chlorides, by suitably heating chlorates.* When sodium chlorate, $NaClO_3$, is gently heated, oxygen is slowly evolved, and if the operation is stopped when one third of the oxygen has been liberated, sodium chloride together with sodium perchlorate remain behind in a fused mass.



$$2\,\mathrm{Na-O-Cl}\begin{matrix}\scriptstyle =O\\ \scriptstyle =O\end{matrix} = \mathrm{Na-O-Cl}\begin{matrix}\scriptstyle =O\\ \scriptstyle =O\\ \scriptstyle =O\end{matrix} + \mathrm{Na-Cl} + \mathrm{O=O}$$

The more soluble sodium chloride may be dissolved out from the mass, leaving the nearly pure sodium perchlorate.

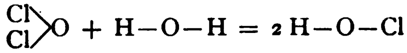
When heated sufficiently, sodium perchlorate is decomposed with formation of sodium chloride and evolution of oxygen.

$$NaClO_4 = NaCl + 2\,O_2$$

Potassium perchlorate, $KClO_4$, may be obtained similarly, and has similar properties.

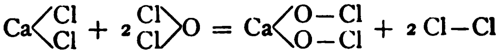
Perchloric Acid. *Perchloric acid may be formed by the action of strong sulphuric acid upon perchlorates.* When sodium perchlorate, $NaClO_4$, is heated with an excess of sulphuric acid, *perchloric acid*, $HClO_4$, and sodium sulphate are formed.

while it will combine explosively with sulphur, carbon, and other ele-ments. When dissolved in water, it forms hypochlorous acid, HClO.



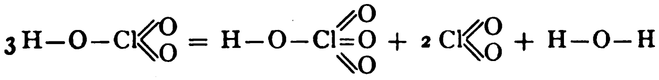
$$\begin{matrix}Cl\\Cl\end{matrix}\!>\!O + H{-}O{-}H = 2\,H{-}O{-}Cl$$

It will oxidize calcium chloride, $CaCl_2$, and other similar chlorides, to corresponding hypochlorates, with evolution of chlorine.



$$Ca\!<\!\begin{matrix}Cl\\Cl\end{matrix} + 2\begin{matrix}Cl\\Cl\end{matrix}\!>\!O = Ca\!<\!\begin{matrix}O-Cl\\O-Cl\end{matrix} + 2\,Cl{-}Cl$$

Chlorine Dioxide. *Chlorine dioxide*, ClO_2, a yellowish green gas, of characteristic odor, soluble in water, readily condensed to a dark red liquid which boils at 9.9° and at −79° forms an orange-colored solid, is a product of the decomposition of chloric acid, $HClO_3$, by heat, perchloric acid and water being formed simultaneously.



$$3\,H{-}O{-}Cl\!\begin{matrix}\nearrow O\\\searrow O\end{matrix} = H{-}O{-}Cl\!\begin{matrix}\nearrow O\\=O\\\searrow O\end{matrix} + 2\,Cl\!\begin{matrix}\nearrow O\\\searrow O\end{matrix} + H{-}O{-}H$$

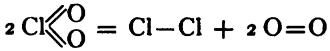
It is produced when potassium chlorate, $KClO_3$, is acted upon by an excess of concentrated sulphuric acid.

$$6\,KClO_3 + 3\,H_2SO_4 = 2\,HClO_4 + 4\,ClO_2 + 2\,H_2O + 3\,K_2SO_4$$

It may be prepared by heating a mixture of potassium chlorate, $KClO_3$, sulphuric acid, and oxalic acid, $H_2C_2O_4$, to 70°, in a water bath, and passing the evolved gases into tubes cooled by a freezing mixture.

$$2\,KClO_3 + H_2C_2O_4 + H_2SO_4 = 2\,ClO_2 + 2\,H_2O + K_2SO_4 + 2\,CO_2$$

The reddish brown liquid thus obtained may be distilled without decomposition if the temperature be kept below 30°. Chlorine dioxide is extremely unstable, decomposing when heated or acted upon by an electric spark with formation of chlorine and oxygen, the decomposition taking place with explosive violence,



$$2\,Cl\!\begin{matrix}\nearrow O\\\searrow O\end{matrix} = Cl{-}Cl + 2\,O{=}O$$

while it reacts explosively with phosphorus, sugar, and similar organic substances. Thus, when strong sulphuric acid is allowed to come in contact with crystals of potassium chlorate under water, without becoming previously diluted by the water, as may be brought about by pouring the sulphuric acid through a tube held immersed in the water *hydroxides; that sulphuric acid decomposes some chlorides, forming hydrogen chloride; that some chlorides of positive elements combine with one another to form double chlorides; and that some chlorides are insoluble and may be formed as precipitates.*

Hypochlorites may be made by the action of chlorine upon basic hydroxides or upon carbonates in excess; may be decomposed by heating, forming chlorides and chlorates and oxygen; and are acted upon by acids, with formation of solutions of hypochlorous acid, which may be similarly decomposed by heating. Hypochlorous acid may also be made in solution by the action of chlorine upon water, best in presence of mercuric oxide, or of certain salts.

Some chlorites, with chlorates, may be made by the action of chlorine dioxide upon basic hydroxides.

Some chlorates may be made by the action of chlorine in excess upon basic hydroxides or upon carbonates; may be decomposed by heating, with formation of chlorides, perchlorates, and oxygen; and are acted upon by acids, with formation of chloric acid, which may be decomposed by heating with evolution of chlorine, or chlorine dioxide, and oxygen.

Perchloric acid may be formed by the action of acids upon perchlorates, and decomposes readily with evolution of oxygen.

Chlorine monoxide may be made by acting upon mercuric oxide with chlorine, and dissolves in water to form hypochlorous acid; chlorine dioxide is made by decomposing chloric acid, and dissolves in water to give an acidic solution from which chlorates and chlorites may be formed: chlorine heptoxide, made by dehydrating perchloric acid, dissolves in water to form perchloric acid. All the chlorine oxides are powerful oxidisers and are explosive.

Manufacturing Processes.

The chlorine compound first in importance technically is *hydrochloric acid*, which is manufactured from sodium chloride principally as a by-product of the Leblanc soda process, and is employed as a source of *chlorine*, which is used in making *solutions of hypochlorites*, *bleaching powder*, *chlorates*, and other compounds, and is also liquefied and used in that condition for many purposes.

Hydrochloric Acid.

We have already seen that the formation of *hydrochloric acid* by the action of sulphuric acid upon sodium chloride takes place in two stages, the first consisting of the formation of sodium hydrogen sulphate,

$$NaCl + H_2SO_4 = NaHSO_4 + HCl$$

hydroxides; that sulphuric acid decomposes some chlorides, forming hydrogen chloride; that some chlorides of positive elements combine with one another to form double chlorides; and that some chlorides are insoluble and may be formed as precipitates.

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acid, the remainder of the chlorine entering into the formation of a waste product, while the *Deacon process* depends upon the oxidizing action of a copper compound, and results in the liberation of nearly all the chlorine. Both processes may be worked continuously, without interruption, the residues of manganese and copper compounds being convertible into the original oxidizing compounds by the action of the air, the conversion of the manganese compound requiring the addition of an outside product, while the copper compound may be converted at the expense of a small amount of heat only.

The Weldon Process. The *Weldon process* is based upon the action of manganese dioxide upon hydrochloric acid, which may consist first in the formation of manganese tetrachloride, $MnCl_4$,

$$4\ HCl + MnO_2 = MnCl_4 + 2\ H_2O$$

which decomposes into manganous chloride, $MnCl_2$, and chlorine,

$$MnCl_4 = MnCl_2 + Cl_2$$

both reactions taking place simultaneously.

$$4\ HCl + MnO_2 = MnCl_2 + Cl_2 + 2\ H_2O$$

In practice other manganese oxides, such as Mn_2O_3 and Mn_3O_4, which may be present in the ores employed, may enter into similar reactions, with evolution of chlorine.

The manganous chloride, $MnCl_2$, formed as a residue, may be oxidized by atmospheric oxygen, in the presence of calcium oxide, at high temperature, with the formation of manganese dioxide, MnO_2, and calcium chloride, $CaCl_2$.

$$2\ MnCl_2 + 2\ CaO + O_2 = 2\ MnO_2 + 2\ CaCl_2$$

In practice, instead of pure manganese dioxide, MnO_2, a residue is recovered which has the composition of *calcium manganite*, $CaMnO_3$, together with some *manganic oxide*, Mn_2O_3, and may be utilized instead of the pure manganese dioxide in the chlorine manufacture. The calcium chloride produced as a final residue, containing one half of the chlorine originally present in the hydrochloric acid, is a waste product. The last part of the process, by which the manganese dioxide destroyed is "recovered" from the manganous chloride residues, makes the process a continuous one, although in the actual working of the process more than half the chlorine of the hydrochloric acid is lost.

In the operation of the Weldon process the *pyrolusite* or other manganese ore employed is mixed with hydrochloric acid in suitably constructed sandstone stills, and heated by jets of steam, when the chlorine evolved passes out through earthenware or leaden pipes, provided with water traps by which the flow of gas may be regulated. The chlorine evolved may be utilized in gaseous form, or may be liquefied and preserved in containers under pressure.

action of chlorine upon calcium hydroxide, $Ca(OH)_2$, in solution results chiefly in the formation of calcium hypochlorite, $Ca(ClO)_2$, when the calcium hydroxide is in excess,

$$2\,Ca(OH)_2 + 2\,Cl_2 = Ca(OCl)_2 + CaCl_2 + 2\,H_2O$$

and of calcium chlorate, $Ca(ClO_3)_2$, when the chlorine is in excess,

$$6\,Ca(OH)_2 + 6\,Cl_2 = Ca(ClO_3)_2 + 5\,CaCl_2 + 6\,H_2O$$

calcium chloride being formed in both cases.

For the production of *calcium hypochlorite*, $Ca(ClO)_2$, the chlorine is allowed to act in the cold upon calcium hydroxide; while to obtain *calcium chlorate*, $Ca(ClO_3)_2$, the chlorination of calcium hydroxide is effected in a hot solution. To obtain *potassium chlorate*, milk of lime at 100° is saturated with chlorine in tanks provided with stirrers, and the resulting liquid is run off into tanks, allowed to settle, and is then treated with an equivalent amount of potassium chloride. The resulting solution is concentrated in iron pans, and the potassium chlorate is allowed to crystallize out from the mother liquor, which is thrown away. The crude crystals may be purified by recrystallization and ground, great care being taken to prevent explosion.

Potassium chlorate is now produced commercially on a very large scale by the electrolysis, under carefully regulated conditions, of a solution of potassium chloride, the potassium separated at the cathode acting upon the water to form hydrogen and potassium hydroxide, which is acted upon by the chlorine, liberated at the anode, to form potassium chlorate in solution.

$$KCl = \overset{+}{K} + \overset{-}{Cl}$$

$$2\,K + 2\,H_2O = 2\,KOH + H_2$$

$$6\,KOH + 3\,Cl_2 = KClO_3 + 5\,KCl + 3\,H_2O$$

Sodium chlorate is produced in a similar manner by the electrolysis of sodium chloride. It is of practical advantage in making potassium chlorate to first produce sodium chlorate by the electrolytic process, and then to act upon it with potassium chloride under definite conditions of concentration.

Bleaching Compounds.

A solution containing the mixed calcium hypochlorite, $Ca(ClO)_2$, and calcium chloride, made by passing chlorine into milk of lime, kept at about 30°, in tanks provided with stirrers, may be used as a *bleach liquor*, but owing to its instability it soon becomes inactive when exposed to the air.

When chlorine gas is absorbed by dry calcium hydroxide, $Ca(OH)_2$, yellowish white *bleaching powder* is obtained, which contains a compound of the composition, $CaCl_2O$, which does not rapidly decompose when allowed to stand exposed to air in dry condition,

$$Ca(OH)_2 + Cl_2 = CaCl_2O + H_2O$$

to a solution of a bromide exceeds a moderate limit, bromine is set free by the oxidizing action of the excess of sulphuric acid upon the hydrogen bromide. Certain other acids, like phosphoric acid, H_3PO_4, which part with their oxygen less easily, act upon bromides even in concentrated solution, to form hydrogen bromide without the separation of bromine.

Hydrogen bromide may also be made by combination of bromine with hydrogen in the presence of spongy platinum or other catalytic agent, and by the action of bromine upon a hydrocarbon, and in other ways.

Hydrogen bromide, HBr, is a colorless gas of specific gravity 80.97, condensing to a liquid at very low temperature, and under great pressure, forming a solid at $-120°$, which melts at $-87°$ and boils at $-73°$. In moist air gaseous hydrogen bromide fumes strongly. It dissolves readily in water, forming a solution which, when saturated at 0°, has a specific gravity of 1.78, and contains 82 per cent. of hydrogen bromide; while at 15° it has a specific gravity of 1.515, and contains 49.8 per cent. of the gas. When a strong solution of hydrobromic acid is boiled, hydrogen bromide is at first evolved, while from a dilute solution nearly pure water is evolved, until the residue contains 48.2 per cent. of the gas, and has a specific gravity of 1.49 at 14°. This solution remains of constant strength, and under 1 atmosphere pressure distils unchanged at 128°, but since its composition is different under different conditions of pressure and temperature, the solution cannot be taken to represent a single definite hydrate of hydrogen bromide. When hydrogen bromide is passed into a saturated solution of the gas at $-20°$, crystals may be formed of the composition $HBr \cdot 2\,H_2O$, which melt at $-11°$.

Hydrogen bromide is a monobasic acid, containing a positive hydrogen-ion, easily replaced by positive elements. The water solution of hydrogen bromide is called *hydrobromic acid.*

The observed specific gravity of hydrogen bromide gas under ordinary conditions corresponds to the molecular symbol HBr, although at high temperatures some dissociation of the molecules into hydrogen atoms and bromine atoms takes place.

Soluble Bromides. *By the action of hydrobromic acid upon basic hydroxides bromides may be formed.* Thus, hydrobromic acid, HBr, gives with sodium hydroxide *sodium bromide*, NaBr, and water,

$$\mathit{Na}-\mathrm{O}-\mathrm{H} + \mathit{H}-\mathrm{Br} = \mathit{Na}-\mathrm{Br} + \mathrm{H}-\mathrm{O}-\mathrm{H}$$

and potassium hydroxide, and other basic hydroxides, may be similarly neutralized by hydrobromic acid with formation of bromides.

Other oxygen compounds, such as chromic acid, H_2CrO_4, and simil acidic hydroxides and their salts, may liberate bromine from hydrobromic acid, and may sometimes oxidize the bromine to bromic acid. We shall find later that bromic acid, $HBrO_3$, and hydrobromic acid, HBr, will interact to set free the bromine contained in both of these compounds.

Hydrobromic acid may be decomposed by electrolysis into hydrogen and bromine.

Hydrogen Bromide and Chlorine. *Hydrogen bromide may be decomposed by the action of free chlorine, with formation of hydrochloric acid and liberation of bromine.* When chlorine is passed into a solution of hydrobromic acid, hydrochloric acid is formed and bromine is set free.

$$2\,H-Br + Cl-Cl = 2\,H-Cl + Br-Br$$

By similar reactions certain chlorides may be reduced to a lower condition of valence by heating with hydrobromic acid.

Bromine may also be formed by decomposing suitable bromides by electricity or by heat, or by the oxidizing action of suitable oxygen compounds, or of chlorine in presence of water; and by the reduction of bromates by suitable agents. Most of the bromine of commerce is made by passing chlorine through solutions of bromides.

Bromine. *Bromine,* discovered by Balard in 1826 in the "bittern" from sea water, is a heavy, reddish brown liquid, of specific gravity 3.18 at 0°, having a characteristic penetrating odor and a powerfully destructive action upon the skin and other animal tissues. It is easily volatile, giving off a heavy, dark brown vapor at ordinary temperatures, and boiling at about 60°, changing into the vapor which has a specific gravity of 159.9. Liquid bromine freezes at −7.3° to a dark brown, easily volatile solid. Bromine is moderately soluble in water, forming a dark brown solution known as *bromine water,* one part of bromine at ordinary temperature being dissolved in 35 parts of water. When bromine water is cooled to 4° there are formed crystals of *bromine hydrate,* $Br_2 \cdot 10\,H_2O$, which decomposes at 6.2°.

Bromine is readily soluble in alcohol, ether, chloroform, and carbon disulphide, forming solutions which, when sufficiently concentrated, possess the characteristic dark brown color of bromine. A small trace of bromine scattered through a large bulk of water solution may therefore be readily detected by adding a few drops of the insoluble ether or

Bromine will combine with the hydrogen of bydrogen sulphide. When a current of hydrogen sulphide, H_2S, is passed through bromine, hydrogen bromide is formed and sulphur is set free.

$$H_2S + Br_2 = 2\,HBr + S$$

By the action of the excess of bromine upon the sulphur, some sulphur bromides may be formed in this process. The hydrogen bromide evolved may be purified from excess of bromine by washing in a solution of hydrogen bromide and potassium bromide containing amorphous phosphorus.

Bromine acts upon hydriodic acid with formation of hydrobromic acid and evolution of iodine.

Bromine and Elements, Oxides, and Hydroxides.

The bromides may also be formed by the action of bromine upon other elements, or upon oxides or hydroxides of certain elements under suitable conditions. When moist bromine and potassium are brought together, ***potassium bromide***, KBr, is formed, sometimes the combination taking place explosively.

$$2\,K + Br_2 = 2\,KBr$$

In dry condition sodium and bromine may be mixed without combination taking place. Many other elements, such as boron, aluminium, antimony, bismuth, phosphorus, and sulphur will combine directly with bromine to form bromides, the reaction in some cases taking place with explosive violence.

When bromine vapor is passed over a mixture of boron trioxide, B_2O_3, and charcoal heated to redness, ***boron tribromide***, BBr_3, is formed as a colorless fuming liquid, while carbon monoxide is evolved.

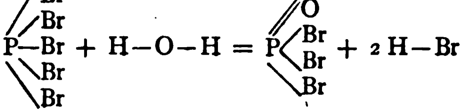
$$B_2O_3 + 3\,Br_2{-}Br + 3\,C = 2\,BBr_3 + 3\,CO$$

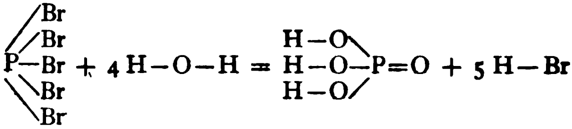
Aluminium tribromide, $AlBr_3$, colorless crystals, and ***silicon tetrabromide***, $SiBr_4$, a heavy liquid, may be made in similar manner by passing bromine over heated mixtures of carbon and aluminium trioxide, Al_2O_3, and silicon dioxide, SiO_2, respectively.

When bromine is added to an excess of a cold solution of sodium hydroxide, a solution of unstable ***sodium hypobromite***, NaBrO, and sodium bromide, NaBr, is formed,

$$2\,Na{-}O{-}H + Br{-}Br = Na{-}Br + Na{-}O{-}Br + H{-}O{-}H$$

but when bromine is added in excess to a hot solution of sodium

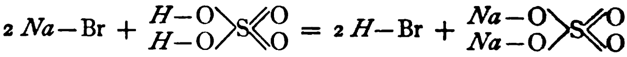




Preparation of Hydrobromic acid. The reaction between phosphorus tribromide, PBr_3, and water is utilized for the preparation of hydrobromic acid for laboratory purposes. To 1 part of water contained in a flask 3 parts of the liquid phosphorus tribromide are gradually added through a thistle-tube, provided with a stopcock, the mixture being gently warmed. The hydrobromic acid gas which is evolved may be washed free of phosphorus tribromide vapor by passing through a U-tube containing glass beads wet with water, and the purified gas may be collected over mercury or dissolved in water. Another process for preparing hydrobromic acid consists in pouring 2 parts of water over red phosphorus and adding 10 parts of bromine, and gently warming the mixture, when the hydrobromic acid gas will be evolved. Or bromine may be allowed to act upon crude anthracene, $C_{14}H_{10}$, or upon naphthalene, $C_{10}H_8$, dissolved in kerosene, when hydrobromic acid will be evolved.

Nitrosyl bromide, NOBr, and *nitroxyl bromide*, NO_2Br, may be made by the combination of bromine with nitrogen dioxide, NO, and *carbon bromide*, $COBr_2$, may be similarly made by the combination of bromine with carbon monoxide.

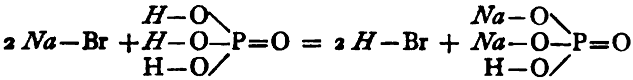
Action of Acids upon Bromides. *Some bromides are decomposed by acids, with the formation of hydrobromic acid, and under certain conditions of free bromine.* Thus, we have seen that in dilute solution sulphuric acid decomposes sodium bromide with formation of a solution of hydrobromic acid, HBr, and sodium sulphate,



and that concentrated sulphuric acid causes the oxidation of the hydrogen with consequent liberation of bromine.

$$2\,NaBr + 2\,H_2SO_4 = Br_2 + 2\,H_2O + SO_2 + Na_2SO_4$$

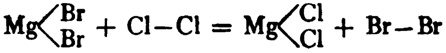
It has also been pointed out that phosphoric acid, H_3PO_4, even in concentrated condition, will act upon sodium bromide to form hydrobromic acid, without separation of bromine.



$$2\,Na{-}Br + \begin{matrix} H{-}O\diagdown \\ H{-}O{-}P{=}O \\ H{-}O\diagup \end{matrix} = 2\,H{-}Br + \begin{matrix} Na{-}O\diagdown \\ Na{-}O{-}P{=}O \\ H{-}O\diagup \end{matrix}$$

Bromides and Chlorine. *Soluble bromides of the metals are decomposed by the action of chlorine, with liberation of bromine and the formation of corresponding chlorides.* If we add to a solution of sodium bromide, or magnesium bromide, chlorine water in small amount, sodium chloride or magnesium chloride will be formed in the solution, which will be colored yellowish or brownish by the bromine which is set free.

$$2\,Na{-}Br + Cl{-}Cl = 2\,Na{-}Cl + Br{-}Br$$



$$Mg\begin{matrix}\diagup Br\\ \diagdown Br\end{matrix} + Cl{-}Cl = Mg\begin{matrix}\diagup Cl\\ \diagdown Cl\end{matrix} + Br{-}Br$$

On adding to the solution slightly colored with bromine a few drops of chloroform or carbon disulphide and thoroughly shaking the mixture, the bromine will be gathered in the small bulk of the chloroform or carbon disulphide, which will assume the characteristic brown color. If an excess of chlorine be added to a water solution of a bromide, the bromine formed as the first product may be oxidized to *bromic acid*, $HBrO_3$, which remains in solution. The action of chlorine upon natural bromides forms the basis of a process by which bromine is manufactured for commercial purposes from the bromides found in the deposits at Stassfurt, which furnish about two thirds of the total product of bromine.

Insoluble Bromides. *The bromides of silver, lead, and mercury in its condition of lowest valence are insoluble and may be produced as precipitates.* When a soluble silver salt such as silver nitrate, $AgNO_3$, is added to a solution of a bromide, such as sodium bromide, we get a precipitate of yellowish white *silver bromide*, AgBr, somewhat acted upon in ammonium hydroxide.

$$NaBr + AgNO_3 = \mathbf{AgBr} + NaNO_3$$

When a solution of lead nitrate, $Pb(NO_3)_2$, or other lead salt is added to a solution of sodium bromide or other bromide, a precipitate of white *lead bromide*, $PbBr_2$, soluble in hot water, is formed.

$$2\,NaBr + Pb(NO_3)_2 = \mathbf{PbBr_2} + 2\,NaNO_3$$

When a solution of a mercurous salt, such as **mercurous** nitrate, $Hg_2(NO_3)_2$, is added to a solution of **sodium bromide** or other bromide, yellowish white *mercurous bromide*, Hg_2Br_2, is precipitated, acted upon by an excess of the reagent.

$$2\,NaBr + Hg_2(NO_3)_2 = \mathbf{Hg_2Br_2} + 2\,NaNO_3$$

Bromides. The *bromides* of most of the elements are soluble in water. The bromides of the alkali and alkali earth elements are white crystalline solids. The most important of these is *potassium bromide*, KBr, which crystallizes in anhydrous cubes and fuses at 740°. It is usually made by acting upon iron with bromine and boiling the resulting iron bromide with potassium carbonate in solution. It is largely used as a medicine, and to some extent in photography. *Sodium bromide*, NaBr, and *magnesium bromide*, $MgBr_2$, found in mineral waters, may be made artificially by similar methods. The bromides of the negative elements are many of them liquids, although some are crystalline solids. Many of them decompose water, as has been shown. Many double bromides containing more than a single positive element are also known.

Oxides and Hydroxides. Bromine does not combine with oxygen directly and no bromine oxide has been formed, although two acidic bromine hydroxides may be formed in solution. Both bromine hydroxides are readily decomposed.

OXIDES	HYDROXIDES
———	Hypobromous acid, HBrO *
———	Bromic acid, $HBrO_3$ *

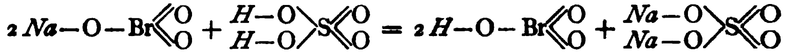
* Known only in solution.

The hypobromites and bromates may be formed by acting upon basic hydroxides or carbonates of positive elements with bromine, and the corresponding hypobromous acid and bromic acid may be formed by acting upon these salts with acids.

Hypobromites and Hypobromous Acid. When **bromine** acts upon **sodium hydroxide** in solution, a colorless solution is obtained which contains sodium bromide, NaBr, mixed with the unstable *sodium hypobromite*, NaBrO, which cannot, however, be separated from the bromide in pure condition.

$$2\,Na-O-H + Br-Br = Na-Br + Na-O-Br + H-O-H$$

When we act upon sodium bromate, $NaBrO_3$, with sulphuric acid, *bromic acid*, $HBrO_3$, is formed in solution,



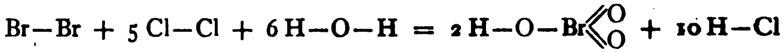
$$2\,Na{-}O{-}Br\begin{smallmatrix}{=}O\\{=}O\end{smallmatrix} + \begin{smallmatrix}H{-}O\\H{-}O\end{smallmatrix}{>}S\begin{smallmatrix}{=}O\\{=}O\end{smallmatrix} = 2\,H{-}O{-}Br\begin{smallmatrix}{=}O\\{=}O\end{smallmatrix} + \begin{smallmatrix}Na{-}O\\Na{-}O\end{smallmatrix}{>}S\begin{smallmatrix}{=}O\\{=}O\end{smallmatrix}$$

and the same acid may also be obtained by acting upon silver bromate, $AgBrO_3$, with bromine water, and removing the insoluble silver bromide, AgBr, by filtration.

$$5\,AgBrO_3 + 3\,Br_2 + 3\,H_2O = 6\,HBrO_3 + 5\,AgBr$$

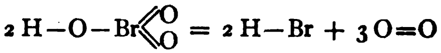
The silver bromate may be formed by acting upon sodium bromate with silver nitrate.

Bromic acid, $HBrO_3$, in solution may also be formed by passing chlorine into bromine water.



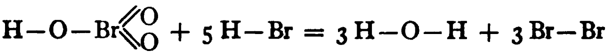
$$Br{-}Br + 5\,Cl{-}Cl + 6\,H{-}O{-}H = 2\,H{-}O{-}Br\begin{smallmatrix}{=}O\\{=}O\end{smallmatrix} + 10\,H{-}Cl$$

Bromic acid, $HBrO_3$, in solution in water, may be somewhat concentrated in a vacuum without decomposing; but it decomposes slowly under ordinary conditions and rapidly when heated, with evolution of oxygen and the formation of hydrobromic acid, HBr,



$$2\,H{-}O{-}Br\begin{smallmatrix}{=}O\\{=}O\end{smallmatrix} = 2\,H{-}Br + 3\,O{=}O$$

which reacts with the bromic acid present in excess, with evolution of bromine.



$$H{-}O{-}Br\begin{smallmatrix}{=}O\\{=}O\end{smallmatrix} + 5\,H{-}Br = 3\,H{-}O{-}H + 3\,Br{-}Br$$

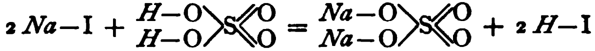
Hydrochloric acid and hydriodic acid will decompose bromic acid, with the formation of chlorine bromide and iodine bromide respectively. Bromic acid is a strong oxidizer and is readily reduced by many substances, with formation of hydrobromic acid, bromine, or bromides.

Summary. *We note that hydrobromic acid forms bromides by interaction with basic hydroxides, carbonates, oxides, and positive elements; that oxygen, free or combined, will liberate bromine from hydrobromic acid; that bromine may combine with hydrogen, free or combined, to form hydrobromic acid; that bromine will combine with other elements, and will react with oxides and hydroxides, to form bromides,*

Production of Iodine. Hydrogen iodide, however, is highly susceptible to the action of oxidizers, and if instead of phosphoric acid an acid capable of exerting an oxidizing action be used, or if an oxidizer be present when the phosphoric acid acts upon the sodium iodide, the hydrogen iodide may be broken up as it forms, with production of water and free iodine.

$$2\,HI + O = H_2O + 2\,I$$

When, for example, the native iodides are heated with a suitable excess of sulphuric acid and manganese dioxide, the first action is to form hydrogen iodide,



$$2\,Na{-}I + \begin{matrix}H{-}O\\ H{-}O\end{matrix}\!\!>\!S\!<\!\!\begin{matrix}O\\ O\end{matrix} = \begin{matrix}Na{-}O\\ Na{-}O\end{matrix}\!\!>\!S\!<\!\!\begin{matrix}O\\ O\end{matrix} + 2\,H{-}I$$

which is at once broken up by the oxygen of the manganese dioxide, free iodine, water, sodium hydrogen sulphate, and manganese sulphate being the final products.

$$2\,NaI + MnO_2 + 3\,H_2SO_4 = 2\,NaHSO_4 + MnSO_4 + 2\,H_2O + I_2$$

Iodine may also be obtained from native iodides, such as sodium iodide, NaI, by electrolysis,

$$(1)\quad 2\,NaI = 2\,Na + I_2$$

$$(2)\quad 2\,Na + 2\,H_2O = H_2 + 2\,NaOH$$

or by the action of chlorine or of bromine,

$$2\,NaI + Cl_2 = 2\,NaCl + I_2$$

$$2\,NaI + Br_2 = 2\,NaBr + I_2$$

and it may also be produced, according to a very important commercial process, by the action of sulphurous acid upon the native sodium iodate, $NaIO_3$, found associated with sodium nitrate.

$$2\,NaIO_3 + 5\,H_2SO_3 = 2\,NaHSO_4 + 3\,H_2SO_4 + H_2O + I_2$$

Iodine. *Iodine*, first prepared by Courtois in 1811 from the ashes of sea plants, and first declared to be an element by Davy and by Gay-Lussac in 1813, is a gray-black, lustrous, crystalline solid, of specific gravity 4.95 at 15°, melting at 114.2° to a dark liquid, and boiling at about 184.3°, with formation of a dark violet vapor of specific gravity 254. Even at ordinary temperatures the iodine crystals give off small quantities of vapor which may be detected by its characteristic violet color and faint odor. Below 600° the specific gravity of iodine vapor correfrom iodides, and thus cause the formation of the blue starch iodide. Strips of unsized paper are dipped in starch emulsion, or in a mixture of starch and potassium iodide solution, dried, and used as *starch test paper* for the detection of the presence of iodine, or of oxidizing substances, either in solution or in gaseous form.

Iodine and Other Elements. *Iodine combines directly with many elements, both electro-positive and electro-negative, to form iodides.* Iodine and potassium when heated together combine with explosive violence to form *potassium iodide*, KI,

$$2\,K + I_2 = 2\,KI$$

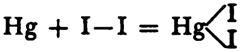
and if a trace of moisture be present, iodine and sodium will similarly combine, forming *sodium iodide*, NaI.

$$2\,Na + I_2 = 2\,NaI$$

Iodine and aluminium combine when heated, forming *aluminium iodide*, AlI_3,

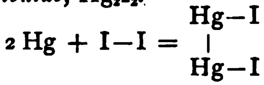
$$2\,Al + 3\,I_2 = 2\,AlI_3$$

and iodine and mercury may be made to combine by rubbing them together to form the red *mercuric iodide*, HgI_2,



$$Hg + I-I = Hg\begin{matrix}\diagup I\\ \diagdown I\end{matrix}$$

or the green *mercurous iodide*, Hg_2I_2.



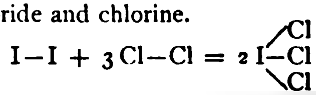
$$2\,Hg + I-I = \begin{matrix}Hg-I\\ |\\ Hg-I\end{matrix}$$

Phosphorus and solid iodine will combine spontaneously when brought in contact, forming *phosphorus iodides*, and finely powdered antimony takes fire in iodine vapor, forming *antimony iodides.*

Iodine and chlorine combine according to the proportions in which they are present to form *iodine monochloride*, ICl, a red crystalline mass, fusing at 24.7°, and boiling at 101.3°,

$$I-I + Cl-Cl = 2\,I-Cl$$

or *iodine trichloride*, ICl_3, yellow crystals, easily decomposed by heat into iodine monochloride and chlorine.



$$I-I + 3\,Cl-Cl = 2\,I\begin{matrix}\diagup Cl\\ -Cl\\ \diagdown Cl\end{matrix}$$

alkali hydroxides to form alkali iodides and secondary products. Thus, iodine acts upon sodium hydroxide to form *sodium iodide*, NaI, together with *sodium hypoiodite*, NaIO, which is converted spontaneously into *sodium iodate*, $NaIO_3$, compounds the relations of which we shall consider later.

$$6\,NaOH + 3\,I_2 = 3\,NaI + 3\,NaIO + 3\,H_2O$$
$$6\,NaOH + 3\,I_2 = 5\,NaI + NaIO_3 + 3\,H_2O$$

The neutral alkali carbonates, such as sodium carbonate, are susceptible to a slight degree to similar reactions.

$$3\,Na_2CO_3 + 3\,I_2 = 3\,NaI + 3\,NaIO + 3\,CO_2$$
$$3\,Na_2CO_3 + 3\,I_2 = 5\,NaI + NaIO_3 + 3\,CO_2$$

Iodine acts upon hydrogen sulphide in water solution to form hydriodic acid and sulphur.

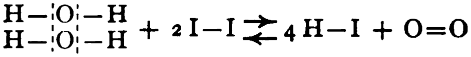
$$I_2 + H_2S = 2\,HI + S$$

Iodine acts upon sodium thiosulphate, $Na_2S_2O_3$, in solution, with formation of sodium iodide and sodium tetrathionate, $Na_2S_4O_6$.

$$2\,Na_2S_2O_3 + I_2 = 2\,NaI + Na_2S_4O_6$$

This action is frequently employed in determining the quantities of free iodine in solutions.

Iodine acts to a very slight extent upon the water in which it is dissolved, with formation of traces of hydriodic acid, and liberation of oxygen, according to the reversible reaction.



$$\begin{array}{l} H-\!\vdots O \vdots\!-H \\ H-\!\vdots O \vdots\!-H \end{array} + 2\,I-I \rightleftarrows 4\,H-I + O=O$$

When, however, a suitable substance possessing an affinity for nascent oxygen is present, the reaction may proceed with the formation of an oxidation product of the substance, and hydrogen iodide or some secondary product of its action.

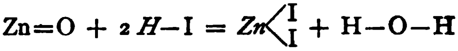
Iodine as an Oxidizer. *Under suitable conditions iodine, while forming an iodide may liberate oxygen from water, and thus act indirectly as an oxidizer.* Iodine acts upon sulphurous acid with formation

Hydrogen Iodide and Other Substances.

Iodides of many elements may be made by the action of hydriodic acid upon suitable hydroxides, oxides, salts of volatile acids, and metals. Thus, hydriodic acid, HI, reacts with sodium hydroxide to form *sodium iodide*, NaI,

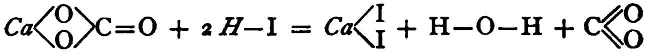
$$Na{-}O{-}H + H{-}I = Na{-}I + H{-}O{-}H$$

with zinc oxide, ZnO, to form *zinc iodide*, ZnI_2,



$$Zn{=}O + 2\,H{-}I = Zn\left\langle\begin{matrix}I\\I\end{matrix}\right. + H{-}O{-}H$$

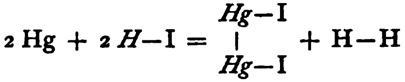
with calcium carbonate to form *calcium iodide*, CaI_2,



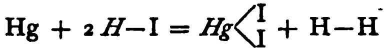
$$Ca\left\langle\begin{matrix}O\\O\end{matrix}\right\rangle C{=}O + 2\,H{-}I = Ca\left\langle\begin{matrix}I\\I\end{matrix}\right. + H{-}O{-}H + C\left\langle\!\!\begin{matrix}=O\\=O\end{matrix}\right.$$

and with the metals silver and mercury, if finely divided, to form the respective iodides, *silver iodide*, AgI, and *mercurous iodide*, Hg_2I_2, or *mercuric iodide*, HgI_2.

$$2\,Ag + 2\,H{-}I = 2\,Ag{-}I + H{-}H$$



$$2\,Hg + 2\,H{-}I = \begin{matrix}Hg{-}I\\ |\\ Hg{-}I\end{matrix} + H{-}H$$



$$Hg + 2\,H{-}I = Hg\left\langle\begin{matrix}I\\I\end{matrix}\right. + H{-}H$$

The reactions between hydriodic acid and the hydroxides, oxides, and carbonates of strongly electro-positive elements, in which water is formed, proceed to completion.

The action of hydriodic acid upon suitable compounds of elements less electro-positive is similar to its action upon similar compounds of more electro-positive elements, but is reversible, and, therefore, less complete. Concentrated hydriodic acid, for example, is able to precipitate *arsenic triiodide*, AsI_3, from a water solution of arsenious acid, H_3AsO_3, and from an arsenite, the acid being formed as an intermediate product, but the reaction is incomplete, and may be completely reversed by increasing the proportion of water present, thus hydrolyzing the arsenic triiodide formed by the direct reaction.

$$H_3AsO_3 + 3\,HI \rightleftarrows AsI_3 + 3\,H_2O$$

A similar effect is produced by the action of strong sulphuric acid upon the water solution of an arsenite and an iodide, precipitation of the arsenic triiodide, AsI_3, taking place when the water simply combines potassium iodide, KI, potassium chloride is formed, and iodine liberated.

$$2\,K-I + Cl-Cl = 2\,K-Cl + I-I$$

Hydriodic acid, HI, is similarly acted upon by chlorine with formation of hydrochloric acid and free iodine.

$$2\,H-I + Cl-Cl = 2\,H-Cl + I-I$$

The addition of bromine to a solution of potassium iodide or of hydriodic acid causes the formation of potassium bromide or of hydrobromic acid, respectively, while iodine is set free

$$2\,K-I + Br-Br = 2\,K-Br + I-I$$
$$2\,H-I + Br-Br = 2\,H-Br + I-I$$

Insoluble iodides are attacked by chlorine and by bromine with more difficulty. The conversion of silver iodide, AgI, into silver chloride, AgCl, by the action of chlorine at high temperature is an example of such action.

$$2\,Ag-I + Cl-Cl = 2\,Ag-Cl + I-I$$

In utilizing as a test for small amounts of iodides the reactions by which iodine is liberated from solutions of iodides by chlorine or bromine, the addition of an excess of these reagents should be avoided, otherwise the iodine first liberated may be at once oxidized to *iodic acid*, HIO_3, by the aid of the water, and so escape observation.

$$I_2 + 5\,Cl_2 + 6\,H_2O = 10\,HCl + 2\,HIO_3$$

Oxidation of Hydrogen Iodide.

Of the iodides, hydrogen iodide is especially susceptible to the action of oxygen, and is acted upon with liberation of iodine by many substances capable of yielding oxygen. Many of the peroxides oxidize the hydrogen of hydriodic acid, free or produced by the interaction of reagents, and are thereby reduced. Manganese dioxide, MnO_2, will oxidize hydriodic acid with liberation of iodine,

$$4\,HI + MnO_2 = MnI_2 + 2\,H_2O + I_2$$

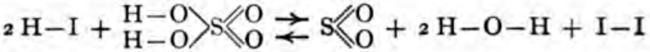
and a mixture of potassium iodide, manganese dioxide, MnO_2, and sulphuric acid, evolves iodine when heated. This is a process by which iodine is made commercially.

$$2\,KI + MnO_2 + 2\,H_2SO_4 = K_2SO_4 + MnSO_4 + 2\,H_2O + I_2$$

and in a mixture of sodium iodide, and sodium dihydrogen arsenate, NaH_2AsO_4, with a suitable amount of sulphuric acid, the reaction proceeds along similar lines.

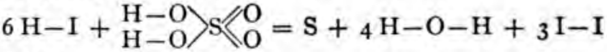
$$2\,NaH_2AsO_4 + 4\,NaI + 3\,H_2SO_4 = 3\,Na_2SO_4 + 2\,H_3AsO_3 + 2\,H_2O + 2\,I_2$$

From antimonic acid, H_3SbO_4, and antimonates, in presence of a strong acid, and an iodide, antimonious acid, H_3SbO_3, and free iodine are obtained. Even sulphuric acid, in concentrated condition, will act upon hydriodic acid, with liberation of iodine and the formation of sulphur dioxide,



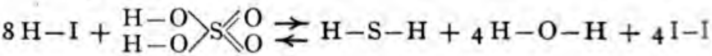
$$2\,\mathrm{H{-}I} + {\mathrm{H{-}O} \atop \mathrm{H{-}O}}\!>\!\mathrm{S}\!<\!{\mathrm{O} \atop \mathrm{O}} \rightleftarrows \mathrm{S}\!<\!{\mathrm{O} \atop \mathrm{O}} + 2\,\mathrm{H{-}O{-}H} + \mathrm{I{-}I}$$

or of sulphur,



$$6\,\mathrm{H{-}I} + {\mathrm{H{-}O} \atop \mathrm{H{-}O}}\!>\!\mathrm{S}\!<\!{\mathrm{O} \atop \mathrm{O}} = \mathrm{S} + 4\,\mathrm{H{-}O{-}H} + 3\,\mathrm{I{-}I}$$

or of hydrogen sulphide.



$$8\,\mathrm{H{-}I} + {\mathrm{H{-}O} \atop \mathrm{H{-}O}}\!>\!\mathrm{S}\!<\!{\mathrm{O} \atop \mathrm{O}} \rightleftarrows \mathrm{H{-}S{-}H} + 4\,\mathrm{H{-}O{-}H} + 4\,\mathrm{I{-}I}$$

Hydriodic acid appears, therefore, to be a reducer of many substances which part with their oxygen readily, and such reducing action may be carried to completion, if the iodine set free from the hydrogen iodide is volatilized from the system. On the other hand, as we have seen, if the conditions are suitable, iodine may be an efficient oxidizer, and the oxidizing action of iodine is promoted by taking care to neutralize the hydrogen iodide formed in the process, as may be done by having present an excess of an acidic alkali carbonate.

Hydriodic Acid as a Reducer. *In some few cases hydriodic acid or soluble iodides may act as reducers, because of the readiness of the positive elements of the compounds acted upon to form similar compounds in which these elements assume a lower valence.* Thus, by heating ferric chloride, $FeCl_3$, with hydriodic acid, ferrous chloride, $FeCl_2$, may be formed,

$$2\,FeCl_3 + 2\,HI = 2\,FeCl_2 + 2\,HCl + I_2$$

and by digesting ferric sulphate, $Fe_2(SO_4)_3$, with potassium iodide solution, ferrous sulphate, $FeSO_4$, may be formed,

$$Fe_2(SO_4)_3 + 2\,KI = 2\,FeSO_4 + K_2SO_4 + I_2$$

the iron in each of the ferric salts acted upon being changed to a condition of lower valence in the ferrous salts formed.

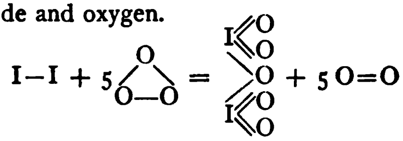
When the acid, like nitric acid or sulphuric acid, is easily reducible, some of the hydriodic acid is decomposed, hydrogen being oxidized to water, and iodine either set free or oxidized. Metal iodides, fused or in solution in water, are easily electrolyzed with evolution of the metal, or a product of its action upon water, at the cathode, and iodine, or a product of its oxidation, at the anode.

Oxides and Hydroxides. Iodine forms but one oxide, but several acidic hydroxides of iodine have been prepared corresponding to unknown oxides, and some salts are known representative of hydroxides which have not been isolated.

OXIDES	HYDROXIDES
——	Hypoiodous acid, HIO *
Iodine pentoxide, I_2O_5	Iodic acid, HIO_3
——	Pentahydroxyl periodic acid, H_5IO_6
	[Monhydroxyl periodic acid, HIO_4] †

* Known in solution. † Represented by salts.

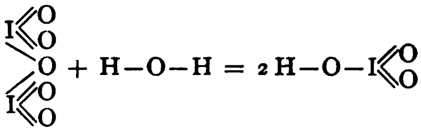
Iodine Pentoxide. *Iodine pentoxide*, I_2O_5 (iodic anhydride), may be formed by the action of ozone upon iodine, or by the dehydration of an iodine hydroxide. Though iodine and ordinary oxygen do not combine with one another, ozone acts upon iodine with the formation of iodine pentoxide and oxygen.



Iodine pentoxide is a white powder, dissociated at 300° into iodine and oxygen.

$$2\,I_2O_5 = 2\,I_2 + 5\,O_2$$

It will unite with water to form *iodic acid*, HIO_3, in solution,



being again formed when iodic acid is heated to 170°. Iodine pentoxide is formed when periodic acid, H_5IO_6, is heated to 140°, and is left when properties by acting upon barium hydroxide, $Ba(OH)_2$, and upon calcium hydroxide, $Ca(OH)_2$, with iodine. We have also certain organic compounds, such as $CH_3-I=O$ and $C_2H_5-I=O$, which resemble the hypoiodites in composition, but are of different constitution.

Iodic Acid. *Iodic acid may be made by acting upon iodine with suitably strong oxidizing agents.* Boiling concentrated nitric acid acts upon iodine to form *iodic acid*, HIO_3, which may be obtained pure by evaporating off the excess of nitric acid, dissolving the residue in water, and evaporating the solution at the ordinary atmospheric temperature in a desiccator.

$$3\,I_2 + 10\,HNO_3 = 6\,HIO_3 + 2\,H_2O + 10\,NO$$

Chlorine in presence of water is capable of converting iodine into iodic acid, hydrochloric acid being formed at the same time.

$$I_2 + 5\,Cl_2 + 6\,H_2O = 2\,HIO_3 + 10\,HCl$$

Even so mild an oxidizer as mercuric oxide, HgO, which in the cold acts upon iodine and water to produce hypoiodous acid, HIO, acts upon iodine and warm water to form iodic acid,

$$6\,I_2 + 5\,HgO + H_2O = 2\,HIO_3 + 5\,HgI_2$$

and iodic acid also results from the spontaneous decomposition of hypoiodous acid produced by the action of these reagents in the cold.

$$5\,HOI = HIO_3 + 2\,I_2 + 2\,H_2O$$

Iodic acid, HIO_3, is a white crystalline solid, of specific gravity 4.63, insoluble in alcohol, and soluble in water, forming a stable solution, decomposing at 170° with evolution of oxygen and formation of iodine pentoxide. It may be made by acting with acids upon the iodates, which, as we shall see, may be made by the action of iodic acid upon bases, and in other ways.

Reduction of Iodic Acid. *Iodic acid in solution is readily reduced with liberation of iodine.* Thus, sulphurous acid, H_2SO_3, acts upon iodic acid, HIO_3, to form sulphuric acid, water, and free iodine.

$$2\,HIO_3 + 5\,H_2SO_3 = I_2 + H_2O + 5\,H_2SO_4$$

Hydrogen sulphide reduces iodic acid with formation of water and liberation of sulphur and iodine.

$$2\,HIO_3 + 5\,H_2S = I_2 + 6\,H_2O + 5\,S$$

the iodates, may be conveniently separated from the iodides by crystallization from solution.

Iodine and Chlorates and Bromates.

Some iodates may be produced by interaction of chlorates or bromates with free iodine. By acting upon sodium chlorate, $NaClO_3$, or upon sodium bromate, $NaBrO_3$, with iodine, *sodium iodate*, $NaIO_3$, is formed, while chlorine or bromine respectively is set free.

$$2\,NaClO_3 + I_2 = 2\,NaIO_3 + Cl_2$$
$$2\,NaBrO_3 + I_2 = 2\,NaIO_3 + Br_2$$

Potassium iodate may be produced similarly by the reaction of potassium chlorate or potassium bromate with iodine.

In these reactions it is to be supposed that the iodine is oxidized at the expense of the chlorate or bromate, and the iodate is the result of the action of iodine oxide upon the metal oxide, chlorine or bromine being liberated, as may be theoretically represented by symbols:

$$2\,NaClO_3 + I_2 = I_2O_5 + Na_2O + Cl_2$$
$$I_2O_5 + Na_2O = 2\,NaIO_3$$

Oxidation of Iodides.

Some iodates may also be produced by the oxidation of iodides in solution. Potassium iodide and potassium permanganate, $KMnO_4$, react in solution to form potassium iodate, KIO_3, and manganese dioxide, MnO_2.

$$KI + 2\,KMnO_4 + H_2O = KIO_3 + 2\,KOH + 2\,MnO_2$$

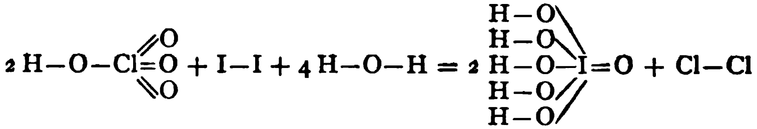
Iodates may also be produced by the reaction between iodides and oxygen produced in the electrolysis of water solutions.

Iodates.

The *iodates* of sodium and of potassium are white salts, sparingly soluble in water, and the iodates of many of the other elements are more insoluble. The most important iodate is *potassium iodate*, KIO_3, which forms small cubical white crystals. It is usually made by treating potassium hydroxide or potassium carbonate with iodine or by oxidizing potassium iodide with potassium permanganate. Compounds of potassium iodate with iodic acid, having the composition $KIO_3 \cdot HIO_3$ and $KIO_3 \cdot 2\,HIO_3$, are also known, and it is possible that they may be acidic salts of a polymeric iodic acid. *Sodium iodate*, $NaIO_3$, similar to potassium iodate, is found associated with the sodium nitrate of the South American deposits. *Barium iodate*, $Ba(IO_3)_2$, *silver iodate*, $AgIO_3$, and *lead iodate*, $Pb(IO_3)_2$, are white insoluble salts which

Iodates in general in neutral solution are very much less susceptible to the action of reducing agents than is iodic acid. Iodates do not react with iodides, for example, in neutral solution, but the addition to such a mixture of a very minute amount of an acid produces iodic acid and hydriodic acid in intermixture, and so liberates iodine. Even the carbon dioxide of the air may cause separation of iodine from a sufficiently exposed mixture of an iodate and an iodide. Neutral mixtures of iodides and iodates are sometimes used to indicate the presence of traces of acids in solutions.

Periodic Acid. *Periodic acid is obtained as the final oxidation product of iodine.* When iodine is acted upon by strong perchloric acid, $HClO_4$, chlorine is evolved, and from the resulting solution colorless deliquescent crystals of *pentahydroxyl periodic acid,* known commonly as *periodic acid,* H_5IO_6, the first product of dehydration of the unknown acid, H_7IO_7, may be obtained.



$$2\,\mathrm{H{-}O{-}Cl(=O)_3} + \mathrm{I{-}I} + 4\,\mathrm{H{-}O{-}H} = 2\,\mathrm{(H{-}O)_5I{=}O} + \mathrm{Cl{-}Cl}$$

Periodic acid, H_5IO_6, melts at 130°, and at 140°, without forming stable intermediate dehydration products, evolves oxygen and water, leaving a residue of iodic acid, HIO_3,

$$2\,H_5IO_6 = 2\,HIO_3 + 4\,H_2O + O_2$$

which upon further heating evolves water, forming iodine pentoxide, I_2O_5, which may be further decomposed into iodine and oxygen.

Periodates. *Periodic acid behaves in solution like a pentabasic acid, forming periodates by neutralization of bases.* With enough sodium hydroxide, for example, periodic acid, H_5IO_6, will form a *pentasodium periodate,* Na_5IO_6,

$$5\,\mathit{Na}\mathrm{OH} + \mathit{H}_5\mathrm{IO}_6 = \mathit{Na}_5\mathrm{IO}_6 + 5\,\mathrm{H_2O}$$

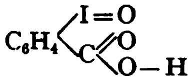
or with less sodium hydroxide the acidic periodates, $Na_3H_2IO_6$, and $Na_2H_3IO_6$, may be obtained.

$$3\,\mathit{Na}\mathrm{OH} + \mathit{H}_3\mathrm{H_2IO_6} = \mathit{Na}_3\mathrm{H_2IO_6} + 3\,\mathrm{H_2O}$$
$$2\,\mathit{Na}\mathrm{OH} + \mathit{H}_2\mathrm{H_3IO_6} = \mathit{Na}_2\mathrm{H_3IO_6} + 2\,\mathrm{H_2O}$$

Oxidation of Iodates. *Periodates may also be made by the oxidation of iodates.* By acting upon sodium iodate, $NaIO_3$, with chlorine in the presence of sodium hydroxide, the pentasodium

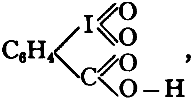
Carbon Compounds containing Iodine.

In connection with the compounds already mentioned, in which iodine enters into combination with oxygen, certain carbon derivatives, because of their related constitution, deserve passing mention. By substituting one of the hydrogen atoms of the hydrocarbon benzene, C_6H_6, with iodine, *phenyl iodide*, C_6H_5-I, may be formed, and this forms with chlorine an addition product known as *phenyliodochloride*, $C_6H_5-I\langle\begin{smallmatrix}Cl\\Cl\end{smallmatrix}$. By acting upon phenyliodochloride with a basic hydroxide, a compound containing oxygen may be formed, known as *iodosobenzene*, $C_6H_5-I=O$, and this, when heated, gives as a product another oxygen compound, *iodoxybenzene*, $C_6H_5-I\langle\!\langle\begin{smallmatrix}O\\O\end{smallmatrix}$. Corresponding to these two compounds, *iodosobenzoic acid*,



$C_6H_4\langle\begin{smallmatrix}I=O\\C\langle\begin{smallmatrix}\!/\!\!/O\\O-H\end{smallmatrix}\end{smallmatrix}$,

and *iodoxybenzoic acid*,



$C_6H_4\langle\begin{smallmatrix}I\langle\!\langle\begin{smallmatrix}O\\O\end{smallmatrix}\\C\langle\begin{smallmatrix}\!/\!\!/O\\O-H\end{smallmatrix}\end{smallmatrix}$,

and their salts are known. All of the *iodoso-* and *iodoxy- compounds* are strong oxidizers, and many of them are explosive. By treating a mixture of iodosobenzene and iodoxybenzene with silver oxide and water, a strongly basic compound known as *diphenyl iodonium hydroxide*, $\begin{smallmatrix}C_6H_5\\C_6H_5\end{smallmatrix}\rangle I-O-H$, is formed, and when this compound is acted upon by an iodide, *diphenyl iodonium iodide*, $\begin{smallmatrix}C_6H_5\\C_6H_6\end{smallmatrix}\rangle I-I$, is precipitated. Many other *iodonium salts*, including insoluble chlorides and bromides and soluble carbonates and nitrates, may be formed. We may consider diphenyl iodonium hydroxide, $\begin{smallmatrix}C_6H_5\\C_6H_5\end{smallmatrix}\rangle I-O-H$, to be a basic hydroxide in close theoretical relation to a hypothetical basic iodine hydroxide, $\begin{smallmatrix}H\\H\end{smallmatrix}\rangle I-O-H$, to which, though unknown, the name *iodonium hydroxide* has been given for purposes of discussion.

Summary.

Iodine combines directly with many elements, both electro-positive and electro-negative, forming iodides; it will combine with hydrogen to form hydrogen iodide, or hydriodic acid; iodides may be formed by the action of iodine upon certain compounds, the iodine taking the electro-positive element, and in some cases by the intervention of water acting indirectly as an oxidizer, with formation of hydriodic acid; iodides may be formed by the action of hydriodic acid upon hydroxides, oxides, salts, and metals; a few insoluble iodides are produced by precipitation; soluble iodides are decomposed by chlorine or bromine

CHAPTER XI

SECONDARY SERIES — GROUP I

Copper, Cu, 63.6
Silver, Ag, 107.93
Gold, Au, 197.2

Secondary Series — Group I. THE elements of Group I of the secondary series are, in many respects, similar to one another. They are all found native in free condition disseminated in rocks, and in combination in rock-forming minerals. They are malleable metals, of high specific gravity, unacted upon by air, without effect upon water, oxidizable with difficulty, copper being the only one of the three capable of direct combination with oxygen. They are acted upon by acids with difficulty, forming salts in which the metals are the positive ions. Gold alone shows a slight tendency to form compounds in which it is a constituent of the negative ion. Copper shows a valence of II in most of its compounds, while the valence of silver is I, and that of gold is I or III.

Copper, silver, and gold are good conductors of electricity. They may be deposited from solutions of their salts by action of the electric current, and by metals above them in the electro-chemical series. Copper, silver, and gold have been known since ancient times, and both the free elements and their alloys find many useful applications, particularly in coinage, and in the manufacture of jewelry and electrical apparatus.

Minerals. In the Lake Superior region of the United States *copper* is found free, disseminated throughout the masses of certain rocks, usually of volcanic origin, in the form of small particles or ramifying masses. Sometimes large isolated masses of copper are found. In Montana and Arizona, and elsewhere, copper is found in minerals, principally in the sulphide *chalcocite*, Cu_2S, and the double sulphides *chalcopyrite*, $CuFeS_2$, and *bornite*, Cu_3FeS_3. Other copper minerals air, make it valuable for many purposes. Sheet copper is largely used for roofing buildings and sheathing ships, and for many purposes of daily life. Next to silver it is the best conductor of electricity, and this property makes copper wire most useful in electrical generators and circuits. It is largely used in electro-plating. Pure copper shrinks when it cools from the molten state, and is therefore not well adapted for making castings.

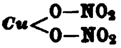
Alloys. Various *alloys* of copper with other metals make good castings, and possess special advantages as to properties. Some of the more useful copper alloys are given in the table.

ALLOYS CONTAINING COPPER

Alloy	Percentage Composition						
	Cu	Zn	Sn	Al	Mn	Ni	P
Brass	50–75	50–25	—	—	—	—	—
Bronze	65–84	31.5–11	2.5–4	—	—	—	—
Gun Metal	91	—	9	—	—	—	—
Aluminium Bronze	90–95	—	—	10–5	—	—	—
Manganese Bronze	70	—	—	—	30	—	—
Phosphorus Bronze	90.5	—	9	—	—	—	.05
German Silver	40–65	19–44	—	—	—	6–32	—

Chemical Behavior. When heated in air or oxygen, copper combines with oxygen and thus forms ultimately a black oxide. In the absence of oxidizing agents dilute hydrochloric acid and dilute sulphuric acid do not attack it, but in presence of air both of these acids will gradually act upon it, and even carbon dioxide in a moist atmosphere will corrode it. Hot concentrated sulphuric acid attacks it, sulphur dioxide being liberated, and it is acted upon readily by nitric acid with evolution of one or more of the oxides of nitrogen, according to the proportion of acid and water acting. Copper is electro-positive and forms two series of salts in which copper is the positive ion.

Copper Oxides. *Copper forms two oxides, the black cupric oxide and the red cuprous oxide.* When a piece of polished sheet copper is very gradually heated in the open air, we notice first the appearance the air, by taking up water to form the hydrous salt. Cupric sulphate is largely used in calico-printing, in the manufacture of pigments, in electroplating, and in electrical batteries.



$Cu<\begin{matrix}O-NO_2\\O-NO_2\end{matrix}$

Cupric nitrate, $Cu(NO_3)_2$, may be made in solution by acting upon copper with nitric acid. When concentrated nitric acid is permitted to act upon copper, violent action takes place, the red fumes of the higher oxides of nitrogen are thrown off, and cupric nitrate remains dissolved.

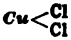
$$Cu + 4\,HNO_3 = Cu(NO_3)_2 + 2\,H_2O + 2\,NO_2$$

If the proportions of the copper and the acid are varied by employing dilute nitric acid, there is an evolution of colorless nitrogen dioxide, NO, which forms red nitrogen trioxide, N_2O_3, on exposure to the air.

$$3\,Cu + 8\,HNO_3 = 3\,Cu(NO_3)_2 + 4\,H_2O + 2\,NO$$

Upon evaporation the green solution yields blue deliquescent crystals, $Cu(NO_3)_2 \cdot 3\,H_2O$, or $Cu(NO_3)_2 \cdot 6\,H_2O$. If crystallized cupric nitrate is heated, water is first evolved, and then the heavy red fumes of nitrogen tetroxide are given off, leaving a black residue of cupric oxide.

$$2\,Cu(NO_3)_2 = 2\,CuO + O_2 + 4\,NO_2$$



$Cu<\begin{matrix}Cl\\Cl\end{matrix}$

Cupric chloride, $CuCl_2$, is formed when cupric oxide, CuO, is acted upon by hydrochloric acid, and very slowly when finely divided copper is boiled with hydrochloric acid in presence of air.

$$CuO + 2\,HCl = CuCl_2 + H_2O$$

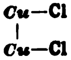
The fairly concentrated solution thus obtained is emerald-green, but when diluted with water it becomes blue. On evaporation of the solution, bright green needles of $CuCl_2 \cdot 2\,H_2O$ are obtained, which turn brown with loss of water when heated. Cupric chloride gives to flame a fine green or blue color sometimes seen in a fire of driftwood which, coming from copper-fastened vessels, is impregnated with copper salts by the action of the sea water upon the copper nails and bolts.

Cupric Hydroxide. *Cupric hydroxide, corresponding to cupric oxide and the cupric salts, may be formed as a precipitate.* If to a solution of sodium hydroxide a solution of cupric sulphate, $CuSO_4$, is added, A solution of potassium ferrocyanide, $K_4Fe(CN)_6$, will precipitate, from a solution of cupric sulphate, *cupric ferrocyanide*, $Cu_2Fe(CN)_6$, of a fine mahogany color.

$$2\,CuSO_4 + K_4Fe(CN)_6 = \mathbf{Cu_2Fe(CN)_6} + 2\,K_2SO_4$$

Cuprous Salts.

By the reduction of cupric salts certain cuprous salts, containing relatively less copper than is present in the cupric salts, may be obtained as precipitates.



$$\begin{matrix}Cu-Cl\\|\\Cu-Cl\end{matrix}$$

Cuprous chloride, Cu_2Cl_2, may be obtained by acting upon cupric chloride, $CuCl_2$, with copper in the presence of hydrochloric acid.

$$CuCl_2 + Cu = \mathbf{Cu_2Cl_2}$$

The operation is best conducted by boiling a solution of cupric chloride containing hydrochloric acid and copper turnings, and pouring the resulting colorless solution into cold water, when the cuprous chloride will be precipitated as finely divided white crystals, which may be acted upon by ammonium hydroxide, with formation of a colorless solution. Cuprous chloride melts at 430°, and vaporizes at 1000°, and its specific gravity, which has been determined at temperatures as high as 1700°, corresponds to the symbol Cu_2Cl_2.

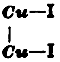
Cuprous chloride in moist air turns green, forming the basic *cupric hydroxychloride*, Cu(OH)Cl.

$$2\,Cu_2Cl_2 + 2\,H_2O + O_2 = 4\,Cu(OH)Cl$$

In the presence of hydrochloric acid, cuprous chloride, on standing in the air, forms cupric chloride.

$$2\,Cu_2Cl_2 + 4\,HCl + O_2 = 4\,CuCl_2 + 2\,H_2O$$

The colorless solution of cuprous chloride in ammonium hydroxide absorbs oxygen rapidly and assumes the blue color characteristic of the cupric ammonia compounds.



$$\begin{matrix}Cu-I\\|\\Cu-I\end{matrix}$$

Cuprous iodide, Cu_2I_2, gray-white, is formed with liberation of iodine when a soluble iodide, such as potassium iodide, KI, is added to a solution of cupric sulphate, $CuSO_4$, or other cupric salt.

$$2\,CuSO_4 + 4\,KI = \mathbf{Cu_2I_2} + 2\,K_2SO_4 + I_2$$

of dark-colored oxyhydroxides, and finally black cupric oxide. Dark blue cupric ammonia compounds may be formed in solution by adding ammonium hydroxide to solutions of cupric salts. Basic cupric carbonates, decomposed by heating, cupric ferrocyanide, and cupric sulphide may also be formed as precipitates.

White insoluble cuprous chloride may be made by heating cupric chloride with copper. It absorbs oxygen and water from moist air, forming cupric hydroxychloride. It absorbs oxygen in the presence of hydrochloric acid, forming cupric chloride. Cuprous iodide may be precipitated by adding a soluble iodide to a solution of a cupric salt.

By the reduction of cupric hydroxide by heating with glucose in presence of the hydroxide of an alkali element, cuprous oxyhydroxide may be formed, which yields cuprous oxide when heated. Copper may be replaced in its salts by the more electro-positive iron and zinc. The copper salts impart a blue or green color to flame.

Metallurgy of Copper. With a knowledge of the chemical reactions of copper and its compounds we may more readily understand the *metallurgical processes* by which copper is obtained from its ores.

Native Copper. When the copper occurs native, the process of refining it is mechanical rather than chemical. The copper-bearing rock is removed by blasting, broken into coarse lumps by crushers, and then passed through *stamps* which hammer it into a coarse sand, from which the lighter particles of rock, known as "tailings," may be washed away by running water. The residue of very nearly pure copper, in the form of coarse granules, is taken to the *smelter*, where it is melted and cast into bars or "ingots" suitable for transportation. This is the method by which copper is obtained in the Lake Superior region in Michigan, where the copper occurs in nearly pure condition, principally in the cement between the small rounded pebbles of conglomerate rock, and as "amygdules" in the cavities of the more solid and massive diabase rock, and occasionally in immense embedded masses. The famous Calumet and Hecla and Tamarack mines, the largest in this region, are the deepest in the world.

The native carbonate ores are first subjected to a preliminary calcining to drive out carbon dioxide and water, and the cupric oxide which is left is then reduced by carbon. In this process of reduction, sand is introduced as a flux to form into a pasty mass the iron oxides and other rocky materials from which the copper oxides cannot be otherwise conveniently separated. Native oxide ores are similarly treated.

Sulphide Ores. The working of sulphide ores of copper consists of a series of roastings in the air to oxidize the sulphur, the melting into sand or other suitable flux to make lighter fusible slags with which is then subjected in a "Bessemer converter" to a blast of air blown through it until the sulphur is all burned out. The *black copper* thus obtained, consisting of copper and cupric oxide, is then cast into plates. These plates, suspended in a solution of cupric sulphate, are made the anodes of an electrolytic cell, the cathodes being copper plates. As the current passes, the copper is removed from the black copper anode and deposits upon the cathodes, the impurities falling to the bottom of the tank. When the copper ores contain silver and gold, as is frequently the case, these metals are found in the mud at the bottom of the tank.

Silver, Ag, 107.93

Occurrence and Properties. Silver is found native in free condition, but more abundantly in compounds. Ordinarily it is a brilliant white metal, soft and ductile. It has a specific gravity of 10.5. It fuses at 960°. It may be crystallized in octahedrons. It is the best conductor of heat and of electricity. It is not oxidized by air or oxygen, and on this account has many uses in the arts.

Varieties of silver are known, however, which appear to be unstable *allotropic forms*. These include the common dark, spongy material, thrown out of the solutions of silver salt by more electro-positive metals, which passes to the condition of white metal, as well as other rare and unstable forms, one of which appears in solution with a blue color, while another is massive with the color of gold. All of these forms take on the characteristics of ordinary silver when heated.

Silver has always been considered a precious metal, and as such has been used in making articles of ornament and in coinage. It is largely used at the present time for electro-plating cheaper metals, and so giving to them a surface of silver. On account of its softness, silver to be used in manufacturing is alloyed with copper. Silver coin generally contains not far from ten per cent. of copper. Silver dissolves in mercury to form an amalgam. Silver is readily acted upon by dilute nitric acid, and is also attacked by hot sulphuric acid and hydrochloric acid. Hydrochloric acid coats it with an insoluble layer of silver chloride. Silver is electro-positive, and forms one series of salts, in all of which it constitutes the positive ion.

Silver Nitrate. *By acting upon silver with nitric acid, silver nitrate may be formed.* If a small piece of silver is heated with nitric acid, diluted with half its volume of water, the acid which evaporates

$\begin{matrix}Ag-O\\Ag-O\end{matrix}>C=O$ *Silver carbonate*, Ag_2CO_3, is a light yellow powder which darkens in the light and when heated. It is formed when a soluble carbonate, such as sodium carbonate, is added to a solution of silver nitrate.

$$2\,AgNO_3 + Na_2CO_3 = \mathbf{Ag_2CO_3} + 2\,NaNO_3$$

$Ag-Cl$ *Silver chloride*, AgCl, is formed as a white precipitate when hydrochloric acid, or a soluble chloride such as sodium chloride, is added to a solution of silver nitrate.

$$AgNO_3 + HCl = \mathbf{AgCl} + HNO_3$$

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The precipitate becomes curdy and settles to the bottom of the liquid upon shaking. It crystallizes in anhydrous octahedra. It is not acted upon by dilute acids. When freshly precipitated, it is readily acted upon by ammonium hydroxide. It is also acted upon by an excess of sodium chloride, and by other alkali chlorides. It turns bluish when exposed to light. It occurs native as the mineral *cerargyrite* (horn silver).

$Ag-Br$ *Silver bromide*, AgBr, is formed as a pale yellow precipitate when a soluble bromide, such as potassium bromide, KBr, is added to a solution of silver nitrate.

$$AgNO_3 + KBr = \mathbf{AgBr} + KNO_3$$

It is acted upon by ammonium hydroxide, though with more difficulty than is silver chloride.

$Ag-I$ *Silver iodide*, AgI, is formed as a yellow precipitate by the action of a soluble iodide, such as potassium iodide, KI, upon a solution of silver nitrate.

$$AgNO_3 + KI = \mathbf{AgI} + KNO_3$$

It is acted upon with much difficulty by ammonium hydroxide.

$\begin{matrix}Ag\\Ag\end{matrix}>S$ *Silver sulphide*, Ag_2S, is precipitated from a solution of silver nitrate by hydrogen sulphide.

$$2\,AgNO_3 + H_2S = \mathbf{Ag_2S} + 2\,HNO_3$$

It is a black, amorphous powder, unacted upon by ammonium hydroxide, but attacked by hot nitric acid. It is also formed as a tarnish on the surface of silver exposed to air containing even small amounts of hydrogen sulphide. The so-called *oxidized silver* is made by exposing silver to sulphur vapor. Silver sulphide also occurs as the mineral *argentite*.

when placed in contact with a piece of zinc. The main reaction may be expressed by the equation,

$$2\,AgCl + Zn = 2\,Ag + ZnCl_2$$

though the hydrogen liberated in the action of the zinc upon the sulphuric acid doubtless takes part in the reaction.

$$2\,AgCl + H_2 = 2\,Ag + 2\,HCl$$

Silver may also be set free from silver compounds by the ionized hydrogen liberated by the electrical current. When silver chloride is melted and then cooled, the solidified mass is found to be a conductor of electricity. When such a mass of compacted silver chloride, $AgCl$, is connected with the negative pole of a battery, and covered with dilute sulphuric acid, into which dips a platinum wire connected with the positive pole of the battery, the hydrogen liberated from the sulphuric acid reduces the silver chloride, depositing silver, and forming hydrogen chloride.

$$2\,AgCl + H_2 = Ag_2 + 2\,HCl$$

The sulphuric acid is decomposed in the process into the hydrogen, which does the reducing, oxygen, which is liberated, and sulphur trioxide, which immediately unites with water to form more sulphuric acid, exactly as we found to be the case when we studied the indirect decomposition of water by electricity.

Summary. *Silver nitrate and silver sulphate, both white fairly soluble salts of silver, may be made by acting upon silver with appropriate acids. By adding a soluble hydroxide to a solution of silver nitrate, a white precipitate of unstable silver hydroxide may be formed, which decomposes spontaneously, forming dark brown sparingly soluble silver oxide. Silver oxide may be acted upon by acetic acid to form silver acetate. Certain insoluble silver salts, such as silver carbonate, silver chloride, silver bromide, silver iodide, silver sulphide, silver chromate, silver cyanide, and silver thiosulphate may be formed as precipitates by adding suitable reagents to solutions of silver salts. Sodium thiosulphate will act upon silver chloride, silver bromide, or silver iodide to form soluble sodium silver thiosulphate. Silver may be replaced in its compounds by more positive metals.*

Photography. Several of the silver salts find a useful application in *photography*. When in contact with organic compounds, silver chloride, silver bromide, and silver iodide, and even silver nitrate, are quickly colored by sunlight, which effects decomposi-

Metallurgy of Silver.

Amalgamation Process.

In the *metallurgy of silver*, the principles which we have studied find useful application. Silver is extracted from its ores by the *amalgamation process*, in which the metal is made into an amalgam with mercury, from which it may be recovered by distilling off the mercury. In countries like Mexico and Peru, where fuel is scarce, the pulverized ore, intimately mixed with a moist mixture of copper sulphate and salt, yields silver chloride, and mercury stirred in at the same time reduces the silver chloride to silver, forming mercury chloride. As mercury is an expensive reagent, the process is much improved as well as simplified by grinding the mixture in iron pans so that the iron may take part in the reaction. In this way the silver chloride is reduced by the iron, and then the mercury amalgamates the silver without waste.

$$2\,AgCl + Fe = 2\,Ag + FeCl_2$$

When fuel is to be had, the silver ore may be roasted with salt to convert it to silver chloride, and then the pulverized material, mixed with water, is reduced by rotating in a barrel with scrap iron. The liquid amalgam, or solution of silver in mercury, purified by straining, is heated in a furnace so constructed that the vaporized mercury may be condensed again. The silver remains as a solid residue.

Concentration and Cupellation Process.

Sometimes silver ores are treated by the *concentration and cupellation process*, in which the ores may be fused directly with lead, which removes the silver from its compounds and forms a lead-silver alloy. In the case of ores poor in silver, it is better to mix the silver ores with lead ores, reducing both simultaneously by suitable furnace treatment, the easily reduced lead carrying with it the silver. In the *lead-silver alloy* thus produced the silver may be concentrated, or brought into smaller bulk, by slowly cooling the fused mass, when the pure lead will crystallize out at the bottom, and may be removed by ladles, leaving finally a readily fusible and very rich alloy of silver and lead; or zinc may be added to the lead-silver alloy, when, upon cooling, there is formed upon the surface a rich zinc-lead-silver alloy, from which the zinc may be removed by distillation. The richer lead-silver alloy thus produced is *cupelled*, or roasted with access of air upon the hearth of a furnace with porous lining. In this process of cupellation the lead is oxidized on the surface of the molten mass and partly volatilized, and partly absorbed by the porous lining of the hearth, the unoxidized silver remaining in the cupel.

Sometimes silver ores are treated by a *precipitation process*. By roasting sulphide ores in air silver sulphate is formed, and the water extract containing the silver sulphate is treated with copper, which deposits the silver.

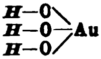
$$Ag_2SO_4 + Cu = 2\,Ag + CuSO_4$$

which at a still higher temperature is dissociated into gold and chlorine.

$$2\,AuCl = 2\,Au + Cl_2$$

The solution of auric chloride in hydrochloric acid, formed when gold is acted upon by aqua regia, yields, on evaporation, yellow needles which contain water of crystallization, and have the composition $HCl \cdot AuCl_3 \cdot 4\,H_2O$, and form well-crystallized salts, like $KCl \cdot AuCl_3 \cdot 2\,H_2O$ and $2(NH_4Cl \cdot AuCl_3) \cdot 5\,H_2O$. Such compounds as these may be considered to be either double salts, or derivatives of a *chlorauric acid*, $HAuCl_4$.

In auric chloride, $AuCl_3$, and other auric compounds, gold is a trivalent positive ion, and in aurous chloride, AuCl, and other aurous compounds, it is a univalent positive ion.



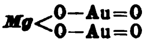
Auric chloride, $AuCl_3$, may be acted upon by a strongly basic hydroxide with formation of *auric hydroxide*, $Au(OH)_3$, or *auric acid*, H_3AuO_3. An excess of the basic hydroxide will neutralize auric acid, forming a compound which has the composition of an oxysalt of auric acid, and may therefore be called an *aurate*. In *auric acid*, H_3AuO_3, and in the aurates, gold is a constituent of the negative ion.

$K-O-Au=O$

Thus, potassium hydroxide added in excess to a solution of auric chloride, $AuCl_3$, will give *potassium aurate*, $KAuO_2$, which may be crystallized out of the solution in bright yellow needles.

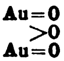
$$AuCl_3 + 3\,KOH = H_3AuO_3 + 3\,KCl$$

$$KOH + H_3AuO_3 = KAuO_2 + 2\,H_2O$$



In the same manner magnesium hydroxide gives *magnesium aurate*, $Mg(AuO_2)_2$.

$$2\,AuCl_3 + 4\,Mg(OH)_2 = Mg(AuO_2)_2 + 4\,H_2O + 3\,MgCl_2$$



By heating magnesium aurate, $Mg(AuO_2)_2$, with dilute nitric acid, *auric acid*, H_3AuO_3, is formed as an insoluble yellow-red powder.

$$Mg(AuO_2)_2 + 2\,HNO_3 + 2\,H_2O = 2\,Au(OH)_3 + Mg(NO_3)_2$$

If concentrated nitric acid is employed in the operation, the auric hydroxide loses its water, and the brown insoluble *auric oxide*, Au_2O_3, remains.

$$Mg(AuO_2)_2 + 2\,HNO_3 = Au_2O_3 + Mg(NO_3)_2 + H_2O$$

Some of the gold compounds find useful application. Auric chloride, and the double chloride of potassium and gold, are largely used in the toning of photographic pictures in silver, as has been previously explained. The solution of the double potassium aurous cyanide is used with a gold anode in the process of *electro-plating* with gold, which depends upon a series of reactions.

$$(1)\qquad KCN\cdot AuCN = \underset{\text{cathode}}{\overset{+}{K}} + \overset{-}{\overbrace{CN\cdot AuCN}}$$

$$(2)\qquad \underset{\text{anode}}{K} + KCN\cdot AuCN = Au + 2\,KCN$$

$$(3)\qquad Au + CN\cdot AuCN = 2\,AuCN$$

$$(4)\qquad KCN + AuCN = KCN\cdot AuCN$$

Finely divided gold and the "purple of Cassius" are used in porcelain painting and in the manufacture of ruby glass.

Summary. *By acting upon gold with chlorine water, or with aqua regia, soluble auric chloride is formed, which, when heated, forms aurous chloride, which, upon further heating, yields gold. By the action upon auric chloride of basic hydroxides in excess, aurates are formed, from which auric acid and auric oxide may be obtained. By the action of a suitable hydroxide upon aurous chloride, aurous oxide may be formed. Auric sulphide and aurous sulphide may be obtained as precipitates. Potassium aurous cyanide, useful in electro-plating, is also known. Gold may be precipitated from its salts by more electro-positive metals and by certain salts.*

Metallurgy of Gold. This *metallurgy of gold* is largely mechanical. The largest repository of gold is the sea water, which appears to contain about 0.0045 grm. of gold to a ton of water, but no method is known for the economic extraction of gold from sea water. Rocks formed upon the sea bottom contain gold, either in the remains of plants which have taken it from the water, or as a deposit by chemical action; and in veins and fissures of metamorphic rocks, filled chiefly with quartz, it is found associated with minerals containing silver, copper, and other metals. In river-drained regions in which the rocky materials of such veins have been broken down by the natural agencies, gold is found in the sand and gravel as "gold dust," and in larger lumps, or "nuggets." *Placer mining* consists in washing away the lighter particles of an auriferous sand or gravel, while saving the heavier gold. The miners, working individually, "pan out" the gold by the rotary motion of water in pans, or, working in pairs, they "cradle" it out; while on the larger scale, methods *hydraulic mining* are employed, the water for the purpose being piped long distances and delivered under great head. The sand and gravel are washed through sluices in which the heavy particles of gold settle, while finer particles are saved by conducting the water over plates covered with mercury which forms an amalgam with gold, just as it does with silver. From such an amalgam the mercury is distilled by heat, while the gold is left behind.

Chlorination and Cyanide Processes. In extracting the gold from rocky and mineral material, the ore is first crushed. In many cases a roasting process follows. At the present time the gold ores containing the gold in free condition, but which do not at the same time contain silver, in fine condition and ready for treatment, are generally either chlorinated or treated by the cyanide process. If the *chlorination process* is used, advantage is taken of the fact that gold is attacked by chlorine, and that the gold may be set free from the compound thus formed by ferrous sulphate. In the *cyanide process* the gold is treated with potassium cyanide in presence of air, and the gold is recovered from the solution by the action of zinc, which forms zinc cyanide and gold. Silver ores often carry a considerable proportion of gold, and if such ores are treated by the amalgamation process, the silver produced contains the gold. In such cases the silver and gold may be "parted" by nitric acid, the silver being removed and the gold remaining; but in order that such "parting" should be successful, the silver must amount to at least three fourths of the whole amount of metal.

The most important gold-producing regions of the world are the United States, Australia, Russia, South Africa, and Alaska. In this country Colorado, California, South Dakota, and Montana rank high as gold-producing states.

CHAPTER XII

SECONDARY SERIES — GROUP II

Zinc, Zn, 65.4
Cadmium, Cd, 112.4
Mercury, Hg, 200.0

Group II.

THE elements of Group II of the secondary series ar lustrous metals, of high specific gravity, and are found i combination in minerals, which occur usually as *ores* in the *veins* of th older crystalline rocks. Cadmium is a rare metal, and its compounds ar found in small quantities associated with the more common ores of z

Properties and Chemical Behavior.

Zinc is a bluish white metal, brittle at ordinary tempe tures, malleable when hot; cadmium is ordinarily malleab mercury is an extremely heavy and mobile liquid. Zinc a cadmium may be melted, and all three metals volatilize high temperatures, and all may be obtained in crystalline conditi Zinc is acted upon superficially by moist air, but cadmium is har affected, and mercury not at all by air at ordinary temperatures, altho all three metals when heated in air form solid insoluble oxides. Ma zinc and cadmium act upon water at red heat, liberating hydrogen, a finely divided zinc will set free hydrogen from water at ordinary te peratures; mercury, however, is without effect upon water.

Zinc, cadmium, and mercury may be deposited from solutions of th salts by the electric current or by metals above them in the elec chemical series, and they will deposit other metals below them in series. Zinc, cadmium, and mercury, and their oxides and hydrox may be acted upon by acids with formation of salts in which these me are positive ions. Mercury forms in this manner two classes of s which differ from each other in the proportions in which mercur contained in them, and cadmium shows to a slight extent a similar te dency to form two classes of compounds; but only one class of zinc s in which zinc is the positive ion, may be formed by the interaction of zinc, or its oxide or hydroxide with common acids. A few zinc salts, in which zinc is in the negative ion, may be formed by the interaction of zinc, or its oxide or hydroxide, with strong basic hydroxides. The valence exhibited by zinc, cadmium, and mercury in their compounds is II.

Minerals. The principal minerals which contain zinc are *sphalerite*, ZnS, *smithsonite*, $ZnCO_3$, *calamine*, $H_2Zn_2SiO_5$, and other more complex compounds. Cadmium is found in the rare mineral *greenockite*, CdS, and small quantities of cadmium are found in combination in the ores in which zinc is the principal metal present. Small quantities of mercury are found in free condition as minute liquid globules disseminated through the pores of certain rocks, and alloys of mercury with gold and silver, known as *amalgams*, are also found native. The principal mineral containing mercury is *cinnabar*, HgS. All three metals of the group may be obtained by roasting their ores, in mixture with carbon when necessary, in suitably constructed retorts or ovens, and condensing the resulting vapors. Both zinc and mercury are important commercial products, and serve many useful purposes.

Zinc, Zn, 65.4

Reduction of Zinc Ores. When the zinc ores, such as the *sphalerite*, ZnS, or *smithsonite*, $ZnCO_3$, are roasted in the air, zinc oxide is formed as a voluminous flocculent yellow powder.

$$2\,ZnS + 3\,O_2 = 2\,ZnO + 2\,SO_2$$
$$ZnCO_3 = ZnO + CO_2$$

By heating with powdered carbon, zinc oxide may be reduced to zinc, which distils, and may be condensed to form compact crude zinc or *spelter*, usually associated with a gray powdery mixture of zinc and zinc oxide known as *zinc dust*.

$$ZnO + C = Zn + CO$$

In the practical *metallurgy of zinc* clay retorts are placed side by side in a furnace and connected with iron receivers. In the *Belgian process* the retorts are tubular in shape and are provided with clay adapters which may be fitted into cylindrical sheet-iron condensers. In the first stage of the heating the escaping carbon monoxide burns with a blue flame at the mouth of the adapter, but when the increased brilliancy the receivers are put in place and the zinc vapor is condensed. In the *Silesian process* rectangular clay muffles, having an arched roof, are employed, and the vapors are led through a bent clay pipe and into an iron tube and an iron tray, in which they are condensed. In either process many retorts may be heated at once. The crude spelter first obtained usually contains lead and iron, and sometimes arsenic and cadmium and other metals, from which it may be removed by repeated distillation. The purified zinc is cast into plates or bars, or rolled in sheets, or dropped in molten condition into water to form *granulated zinc*, useful in the laboratory because of the large surface which it presents. In this country the principal zinc mines are in Missouri, Kansas, New Jersey, and Pennsylvania, while abroad most of the zinc is mined in Belgium, Germany, Great Britain, and Spain.

Zinc. *Zinc* is a bluish white metal, of rough crystalline fracture, having a specific gravity of 7–7.1, melting at 420°, and at about 950° forming a vapor of specific gravity 65.5, corresponding to the monatomic molecular symbol Zn. At ordinary temperatures and above 200° zinc is brittle, and can be readily pulverized, but at 100°–150° it is malleable and ductile, and can be rolled into sheets or drawn into wire. By pouring away the liquid portion from a mass of molten zinc which has begun to cool, prismatic crystals of zinc may be obtained. When solid zinc stands in moist air, it becomes covered with a white coating of a basic zinc carbonate, and when sufficiently heated in air it burns with a bluish white flame with formation of the oxide. At red heat massive zinc attacks water, liberating hydrogen and forming the oxide, and finely divided zinc may act slowly upon water at ordinary temperature. Impure zinc, containing traces of other metals, is readily acted upon by the common dilute acids, and by basic hydroxides, with formation of salts, and usually, except in the case of nitric acid, with evolution of hydrogen. Pure zinc, however, is slowly attacked by acids and by bases.

Uses of Zinc. Zinc is largely employed for industrial purposes and as a reagent in the laboratory. Because of the difficulty with which it is acted upon by water, sheet zinc is used as a lining for vessels of various kinds, while iron vessels are *galvanized* by being cleaned, plunged into molten zinc, and thus covered with a thin coating of zinc which renders them rust proof. Zinc is also largely employed as

The reaction between zinc and dilute sulphuric acid is sometimes used for the preparation of hydrogen, the zinc sulphate formed remaining in solution and thus not interfering with the completion of the reaction. If too concentrated sulphuric acid be employed, however, zinc sulphate, insoluble under the conditions, may form a protecting coat about the particles of zinc, and thus retard the action.

When the solution of zinc sulphate is evaporated, white prismatic crystals of specific gravity 1.95, of the composition $ZnSO_4 \cdot 7\ H_2O$, are obtained. These crystals at 100° lose six equivalents of water, becoming $ZnSO_4 \cdot H_2O$, and at red heat become anhydrous $ZnSO_4$, of specific gravity 3.4. A salt of the composition $ZnSO_4 \cdot 6\ H_2O$, and various double salts with alkali sulphates, such as $K_2SO_4 \cdot ZnSO_4 \cdot 6\ H_2O$, are also known.

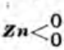
The anhydrous zinc sulphate, when strongly heated, evolves sulphur trioxide, leaving finally a residue of zinc oxide,

$$ZnSO_4 = ZnO + SO_3$$

while it may be completely reduced by carbon or other reducing agent with formation of zinc.

$$ZnSO_4 + C = Zn + CO_2 + SO_2$$

The crystallized zinc sulphate, $ZnSO_4 \cdot 7\ H_2O$, or "white vitriol," manufactured by roasting zinc sulphide ores in the air, extracting the residues with water, and crystallizing the salt from the solution, is employed in dyeing and in medicine.



$$Zn{<}\begin{matrix}O-NO_2\\O-NO_2\end{matrix}$$

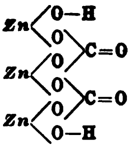
Zinc nitrate, $Zn(NO_3)_2$, may be formed in solution by acting with nitric acid upon zinc, with the simultaneous formation of nitrogen oxides, nitrogen, hydroxylamine, or ammonia according to the conditions of dilution of the nitric acid employed.

$$Zn + 4\ HNO_3 = Zn(NO_3)_2 + 2\ H_2O + 2\ NO_2$$
$$2\ Zn + 6\ HNO_3 = 2\ Zn(NO_3)_2 + 3\ H_2O + N_2O_3$$

By evaporating the solution obtained by acting upon zinc with nitric acid in any proportion, crystals may be obtained of the composition $Zn(NO_3)_2 \cdot 6\ H_2O$. When these are heated, water and nitric acid are evolved and various basic nitrates are formed, while, by very strong heating, nitrogen oxides are evolved and a residue of zinc oxide remains

$$2\ Zn(NO_3)_2 = 2\ ZnO + O_2 + 4\ NO_2$$

Insoluble Zinc Salts. *Some insoluble salts of zinc, in which zinc is electro-positive, may be precipitated from solutions of zinc salts.*



By adding to a solution of zinc sulphate, $ZnSO_4$, or of any other zinc salt, a soluble carbonate, such as sodium carbonate, a white precipitate is formed of a basic zinc *hydroxycarbonate* of variable composition, which becomes more basic as the temperature is raised. The symbol $Zn_3(OH)_2(CO_3)_2$ represents the composition of such a basic zinc carbonate of common occurrence.

$$3\,ZnSO_4 + 3\,Na_2CO_3 + H_2O = \mathbf{Zn_3(OH)_2(CO_3)_2} + CO_2 + 3\,Na_2SO_4$$

When the dried precipitate is strongly heated, carbon dioxide and water are evolved, and zinc oxide is formed,

$$Zn_3(OH)_2(CO_3)_2 = 3\,ZnO + 2\,CO_2 + H_2O$$

and when it is acted upon by sulphuric acid, carbon dioxide and water are evolved, and zinc sulphate is formed in solution,

$$Zn_3(OH)_2(CO_3)_2 + 3\,H_2SO_4 = 3\,ZnSO_4 + 4\,H_2O + 2\,CO_2$$

and the action of other acids is similar.

A large number of basic zinc carbonates may be prepared artificially by the action of reagents upon zinc compounds under suitable conditions. The neutral *zinc carbonate*, $ZnCO_3$, occurs native as the mineral *smithsonite*.

Zn=S When ammonium sulphide, $(NH_4)_2S$, or any sulphide of an alkali element, is added to a solution of zinc sulphate, $ZnSO_4$, or of any other zinc salt, a white precipitate of a hydrated zinc *sulphide*, $ZnS \cdot H_2O$ is formed,

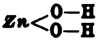
$$ZnSO_4 + (NH_4)_2S + H_2O = \mathbf{ZnS \cdot H_2O} + (NH_4)_2SO_4$$

which is readily acted upon by sulphuric acid, and by other common acids with formation of zinc salts and hydrogen sulphide.

$$ZnS \cdot H_2O + H_2SO_4 = ZnSO_4 + H_2S + H_2O$$

Hydrogen sulphide precipitates hydrated zinc sulphide from a solution of zinc acetate, but precipitation is only partial from salts of the stronger acids. Upon heating the hydrated zinc sulphide, a mixture of anhydrous zinc sulphide, ZnS, and zinc oxide is formed.

Zinc Hydroxide.



$$Zn<\begin{matrix}O-H\\O-H\end{matrix}$$

By the action upon soluble zinc salts of strong basic hydroxides, zinc hydroxide may be precipitated. By adding sodium hydroxide, or any other soluble basic hydroxide, to a solution of zinc sulphate, $ZnSO_4$, or of any other zinc salt, we may precipitate white *zinc hydroxide*, $Zn(OH)_2$, readily acted upon by an excess of basic hydroxides and by acids.

$$ZnSO_4 + 2\,NaOH = \mathbf{Zn(OH)_2} + Na_2SO_4$$

When the dried precipitate of zinc hydroxide is heated, water is evolved and zinc oxide results.

$$Zn(OH)_2 = ZnO + H_2O$$

When zinc hydroxide is acted upon by sulphuric acid, zinc sulphate is formed,

$$Zn(OH)_2 + H_2SO_4 = ZnSO_4 + 2\,H_2O$$

and other acids similarly act upon it to form corresponding salts.

When zinc hydroxide is acted upon by sodium hydroxide, unstable sodium zincate, $NaZnO_2$, is formed in solution,

$$2\,NaOH + Zn(OH)_2 = Na_2ZnO_2 + 2\,H_2O$$

and potassium hydroxide and ammonium hydroxide act upon it similarly.

Since zinc is a strongly electro-positive element, standing above most of the common metals in the electro-chemical series, it will replace most of the common metals in solutions of their salts. Thus, we have seen that strips of zinc plunged into solutions of the salts of copper, silver, or gold, will spontaneously decompose these compounds, becoming covered with coatings of these respective metals in a state of fine division, while corresponding salts of zinc are formed in solution.

Summary.

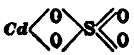
Zinc oxide may be formed by heating zinc in air; by the action upon zinc or zinc oxide of the corresponding acids, zinc sulphate, zinc nitrate, and hydrated zinc chloride may be formed respectively; by heating zinc sulphate or zinc nitrate, zinc oxide may be formed; and by heating hydrated zinc chloride, some basic zinc chloride, or zinc hydroxide, or zinc oxide, as well as anhydrous zinc chloride, results; basic zinc carbonates, decomposable by heat with formation of zinc oxide, and by acids with formation of corresponding zinc salts, may be precipitated from solutions of zinc salts by soluble carbonates; hydrated zinc sulphide, changeable into zinc oxide by heating in air, and decomposable by acids with formation of corresponding zinc salts, may be precipitated hedral crystals of microscopic size when sublimed at white heat. It has a specific gravity of 6.5, and is insoluble in water. It may be acted upon by carbon as other reducing agents with formation of cadmium, which under suitable conditions may be obtained in free condition.

$$CdO + C = Cd + CO$$

Another oxide of cadmium, known as *cadmous oxide*, Cd_2O (cadmium suboxide), has been obtained as yellow crystals by heating cadmous hydroxide. It acts as a reducing agent, readily forming cadmium oxide, CdO, at the expense of the oxygen of other substances.

Soluble Cadmium Salts.

By the action of strong acids upon cadmium or cadmium oxide, corresponding cadmium salts may be formed.



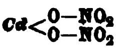
Cadmium sulphate, $CdSO_4$, is formed slowly in solution by the action of sulphuric acid upon cadmium,

$$Cd + H_2SO_4 = CdSO_4 + H_2$$

and more readily by the action of sulphuric acid upon cadmium oxide, CdO.

$$CdO + H_2SO_4 = CdSO_4 + H_2O$$

When the water solution is allowed to evaporate at ordinary temperature, crystals of the composition $3\,CdSO_4 \cdot 8\,H_2O$ may be obtained, although at — 20° crystals have been obtained having the composition $CdSO_4 \cdot 7\,H_2O$ and $CdSO_4 \cdot H_2O$. Basic cadmium sulphates are also known. Cadmium sulphate forms double salts with the alkali sulphates, such as $Na_2SO_4 \cdot CdSO_4 \cdot 2\,H_2O$, $K_2SO_4 \cdot CdSO_4 \cdot 2\,H_2O$, and $K_2SO_4 \cdot CdSO_4 \cdot 6\,H_2O$. At a white heat the cadmium sulphates are converted completely into cadmium oxide.

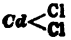


$Cd<\begin{smallmatrix}O-NO_2\\O-NO_2\end{smallmatrix}$

Cadmium nitrate, $Cd(N_3O)_2$, may be obtained in solution by acting with nitric acid upon cadmium or cadmium oxide, CdO.

$$Cd + 4\,HNO_3 = Cd(NO_3)_2 + 2\,H_2O + 2\,NO_2$$

It forms deliquescent crystals of the composition $Cd(NO_3)_2 \cdot 4\,H_2O$, which may be decomposed by heating and by sulphuric acid.



$Cd<\begin{smallmatrix}Cl\\Cl\end{smallmatrix}$

Cadmium chloride, $CdCl_2$, may be made by the action of hydrochloric acid upon cadmium or cadmium oxide.

$$Cd + 2\,HCl = CdCl_2 + H_2$$
$$CdO + 2\,HCl = CdCl_2 + H_2O$$

which gives cadmium oxide, CdO, when heated,

$$Cd(OH)_2 = CdO + H_2O$$

and may be acted upon by acids with formation of corresponding cadmium salts, sulphuric acid acting upon it to give cadmium sulphate, $CdSO_4$.

$$Cd(OH)_2 + H_2SO_4 = CdSO_4 + 2\ H_2O$$

Another hydroxide of cadmium, *cadmous hydroxide*, CdOH, may be formed by the action of water upon certain complex halogen compounds of cadmium, such as Cd_4Cl_7, Cd_4Br_7, or Cd_2I_{23}, obtained by volatilizing the ordinary halogen compounds, $CdCl_2$, $CdBr_2$, CdI_2, over cadmium. It is a grayish white unstable substance, which gives *cadmous oxide*, Cd_2O, upon heating. Cadmous oxide acts as a reducer.

Cadmium, being less electro-positive than zinc, may be replaced by zinc from solutions of cadmium salts. When we plunge a piece of zinc into a concentrated solution of cadmium sulphate, $CdSO_4$, the zinc becomes covered with a dark coating of finely divided cadmium, while zinc sulphate is formed in solution.

$$CdSO_4 + Zn = Cd + ZnSO_4$$

Magnesium may also replace cadmium from its salt solutions, while cadmium will itself replace copper, silver, gold, and many other common metals from solutions of their salts.

Summary. *Cadmium oxide may be formed by heating cadmium in air, and cadmous oxide may be obtained by heating cadmous hydroxide; by the action of the corresponding acids upon cadmium or cadmium oxide, cadmium sulphate, cadmium nitrate, and cadmium chloride may be formed; cadmium carbonate, decomposable by heating and by acids, and cadmium sulphide, may be precipitated from solutions of cadmium salts; cadmium hydroxide may be precipitated by adding soluble hydroxides to solutions of cadmium salts, while cadmous hydroxide may be formed by the hydrolysis of certain complex halogen compounds of cadmium; cadmium may be replaced in solutions of its salts by zinc and some other more positive elements, and will itself replace copper, silver, gold, and other positive elements from their salts.*

impurities rise as a scum to the surface, and may be strained out by squeezing the metal through chamois skin. Mercury may also be freed from impurities by distilling it, best under diminished pressure.

Uses of Mercury. Because of its specific gravity, its stability in air and water, and the ease with which it may be obtained in pure condition mercury is largely employed in making scientific instruments. It is used in the *barometer*. Its uniform rate of change in volume with changing temperature, together with its low freezing point and high boiling point, adapts mercury for use in *thermometers*. Its high electrical conductivity makes it useful in the construction of many forms of electrical apparatus.

Mercury is largely employed in the metallurgical processes for the separation of silver and gold from their ores, since mercury forms with these elements *amalgams*, from which the mercury may be driven by heating. *Sodium amalgam* is used in metallurgy and is also valuable as a reducing agent in many laboratory processes. *Copper amalgam* is used for sealing glass vessels, and tin *amalgam* is used for "silvering" glass plates, in the manufacture of mirrors.

Oxides and Salts. Mercury forms two oxides, mercuric oxide, HgO, and mercurous oxide, Hg_2O, and corresponding to these two oxides there are two series of mercury salts — the *mercuric salts* and the *mercurous salts*, which differ from each other in the proportions in which mercury enters into their composition, the mercurous salts containing the larger proportion of mercury, and the mercuric salts the smaller proportion of mercury, as compared with the fixed amounts of the negative ions present.

MERCURIC COMPOUNDS	MERCUROUS COMPOUNDS
Mercuric oxide, HgO	Mercurous oxide, Hg_2O
Mercuric nitrate, $Hg(NO_3)_2$	Mercurous nitrate, $Hg_2(NO_3)_2$
Mercuric sulphate, $HgSO_4$	Mercurous sulphate, Hg_2SO_4
Mercuric chloride, $HgCl_2$	Mercurous chloride, Hg_2Cl_2

Mercuric Oxide. *Mercuric oxide may be made by heating mercury in air or oxygen.*

$Hg=O$ *Mercuric oxide*, HgO, is a bright red crystalline powder of specific gravity 11.2, or a yellow amorphous powder, according to the mode of preparation. The red mercuric oxide may be made by subjecting mercury to prolonged heating in air at a temperature below the boiling point, when the minute crystals form in gradually increasing quantity on the surface of the mercury,

$$2\,Hg + O_2 = 2\,HgO$$

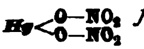
or by heating a mixture of mercuric nitrate and mercury. The yellow variety of mercuric oxide is formed as a slightly soluble precipitate by acting with an excess of an alkali hydroxide upon a solution of mercuric nitrate or mercuric chloride. When heated, mercuric oxide darkens, and at 400° decomposes into mercury and oxygen, a partial recombination of the two elements occurring on cooling the product.

$$2\,HgO \rightleftarrows 2\,Hg + O_2$$

This reaction, used by Priestley in 1774 in his discovery of oxygen, is still employed for producing oxygen for laboratory purposes.

Many finely divided metals are oxidized when heated with mercuric oxide. A mixture of sulphur and mercury oxide explodes when heated. Mercuric oxide is readily attacked by hydrochloric acid and by nitric acid with formation of salts in solution. Mercuric oxide may be acted upon by liquid ammonia and by ammonium hydroxide to form certain unstable dimercurammonium compounds.

Mercuric Salts. *The mercuric salts may be made by acting with strong acids in excess upon mercury or upon mercuric oxide, and a few may be formed as precipitates.*


$\mathrm{Hg}\!<\!\begin{array}{l}\mathrm{O{-}NO_2}\\ \mathrm{O{-}NO_2}\end{array}$

Mercuric nitrate, $Hg(NO_3)_2$, may be made by acting with an excess of nitric acid upon mercury.

$$Hg + 4\,HNO_3 = Hg(NO_3)_2 + 2\,H_2O + 2\,NO_2$$

or by the interaction of nitric acid and mercuric oxide.

$$HgO + 2\,HNO_3 = Hg(NO_3)_2 + H_2O$$

From the resulting solutions, containing an excess of nitric acid, deliquescent crystals of the composition $2\,Hg(NO_3)_2 \cdot H_2O$ may be obtained by evaporation over sulphuric acid at ordinary temperature. At −15° the salt holds eight equivalents of water, and is represented by the symbol $Hg(NO_3)_2 \cdot 8\,H_2O$.

Mercuric nitrate, $Hg(NO_2)_2$, does not dissolve in pure water without residue, and the clear solution which may be made, if a little nitric acid is present, becomes turbid on dilution with water, because of the formation of various insoluble mercuric oxynitrates, which approximate more or less to the composition of mercuric oxide, and which by a sufficiently extended treatment with water leave mercuric oxide as a final residue. Such a *mercuric oxynitrate,* formed as an intermediate product of the hydrolysis of mercuric nitrate, has the composition $Hg_3O_2(NO_3)_2 \cdot H_2O$.

$$3\,Hg(NO_3)_2 + 2\,H_2O = Hg_3O_2(NO_3)_2 + 4\,HNO_3$$

By the action of water upon this compound, mercuric oxide is left as a final residue,

$$Hg_3O_2(NO_3)_2 + H_2O = 3\,HgO + 2\,HNO_3$$

so we may represent the complete action of water upon mercuric nitrate as forming nitric acid and a residue of mercuric oxide.

$$Hg(NO_3)_2 + H_2O = HgO + 2\,HNO_3$$

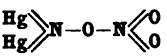
When mercuric nitrate is carefully heated, nitrogen tetroxide and oxygen are evolved, and a residue of mercuric oxide is left behind.

$$2\,Hg(NO_3)_2 = 2\,HgO + O_2 + 4\,NO_2$$

If a mixture of mercuric nitrate and mercury is heated similarly, all the mercury is converted into mercuric oxide, and nitrogen dioxide is formed.

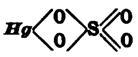
$$Hg(NO_3)_2 + 3\,Hg = 4\,HgO + 2\,NO$$

This is a commercial method for manufacturing mercuric oxide. When a solution of mercuric nitrate containing some nitric acid is shaken with mercury, the reducing action of the mercury proceeds only to the formation of mercurous nitrate.



When ammonium hydroxide is added to a hot dilute solution of mercuric nitrate, $Hg(NO_3)_2$, *dimercurammonium nitrate,* NHg_2NO_3, may be formed as a white insoluble precipitate.

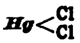
$$2\,Hg(NO_3)_2 + 4\,NH_4OH = NHg_2NO_3 + 3\,NH_4NO_3 + 4\,H_2O$$



Mercuric sulphate, $HgSO_4$, may be prepared as a white crystalline mass by heating mercury with sulphuric acid and evaporating the excess of acid, sulphur dioxide being evolved.

$$Hg + 2\,H_2SO_4 = HgSO_4 + 2\,H_2O + SO_2$$

Upon covering this anhydrous salt with exactly the equivalent amount of water, the mass is changed to colorless brilliant crystals having the composition $HgSO_4 \cdot H_2O$, which by further action of water yield the yellow insoluble basic sulphate $Hg_3O_2(SO_4)$. Mercuric sulphate is acted upon by sulphuric acid in excess, probably with the formation of an acidic mercuric sulphate.


$Hg<^{Cl}_{Cl}$

Mercuric chloride, $HgCl_2$ (corrosive sublimate), may be made by the direct action of an excess of chlorine upon mercury, or by other reactions in which mercury and chlorine are brought into action indirectly in suitable proportions. It is formed when chlorine is passed over mercury heated to boiling point,

$$Hg + Cl_2 = HgCl_2$$

by acting upon mercuric oxide, HgO, with hydrochloric acid,

$$HgO + 2\,HCl = HgCl_2 + H_2O$$

and by heating mercuric sulphate, $HgSO_4$, and sodium chloride in mixture, advantage being taken of the fact that mercuric chloride is volatile at moderately high temperature.

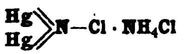
$$HgSO_4 + 2\,NaCl = HgCl_2 + Na_2SO_4$$

The last process is a commercial method for the preparation of mercuric chloride.

Mercuric chloride, $HgCl_2$, is a white crystalline substance of specific gravity 5.4, melting at 265°, boiling at 307°, moderately soluble in cold water, readily soluble in hot water and in alcohol, from which it may be crystallized. The specific gravity of mercuric chloride vapor corresponds to the symbol $HgCl_2$. Mercuric chloride is an active poison, and is largely used as a disinfectant and in surgery as an antiseptic.

Mercuric chloride may be reduced to mercurous chloride by mercury, stannous chloride, sulphurous acid, and other reducing agents.

Mercuric chloride combines with mercuric oxide to form the compounds $2\,HgCl_2 \cdot HgO$, $HgCl_2 \cdot 2\,HgO$, etc., with hydrochloric acid to form $HgCl_2 \cdot HCl$ and $2\,HgCl_2 \cdot HCl$, and with the alkali chlorides or ammonium chloride to form $KCl \cdot HgCl_2 \cdot H_2O$, $2\,KCl \cdot HgCl_2 \cdot H_2O$, $2\,NaCl \cdot HgCl_2$, $NH_4Cl \cdot HgCl_2$, and many other similar complex salts.


$^{Hg}_{Hg}\!>\!N{-}Cl \cdot NH_4Cl$

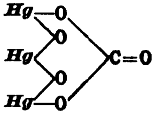
When ammonium hydroxide is added to a solution of mercuric chloride, an insoluble dimercurammonium derivative is formed, which has the composition $NHg_2Cl \cdot NH_4Cl$, correammonium chloride, and known as "infusible white precipitate."

$$2\,HgCl_2 + 4\,NH_4OH = NHg_2Cl \cdot NH_4Cl + 2\,NH_4Cl + 4\,H_2O$$

Another similar double salt, $NHg_2Cl \cdot 3\,NH_4Cl$, known as "fusible white precipitate," may be made by heating the "infusible white precipitate" with ammonium chloride.

Mercuric bromide, $HgBr_2$, is a crystalline solid, formed by the action of bromine upon mercury, or of hydrobromic acid upon mercuric oxide.

Mercuric iodide, HgI_2, is a dimorphous crystalline substance, scarlet or yellow, according to the temperature and mode of crystallization. It is made by rubbing together an excess of iodine with mercury, best in presence of alcohol, or by adding a soluble iodide to a solution of a mercuric salt. Potassium iodide precipitates from solutions of mercuric chloride, yellow mercuric iodide, and this changes to scarlet. From its solution in methylene iodide, mercuric iodide crystallizes in the yellow form or in the red form, according to temperature. When the dry red mercuric iodide is heated above the transition temperature, 126°, it goes over suddenly to the yellow form, and on further heating a portion sublimes in yellow needles, a portion fusing at 223° to a red liquid. The yellow form when rubbed passes into the red form, with evolution of heat. Many double iodides of mercury and other elements, such as $HgI_2 \cdot HI$, $2\,HgI_2 \cdot 3\,HI$, $HgI_2 \cdot KI$, $HgI_2 \cdot 2\,KI$, etc., are known.



A solution of mercuric nitrate, $Hg(NO_3)_2$, gives when acted upon by a soluble carbonate, such as sodium carbonate, a reddish brown precipitate of a *mercuric oxycarbonate*, which approximates the composition $Hg_3O_2CO_3$.

$$3\,Hg(NO_3)_2 + 3\,Na_2CO_3 = Hg_3O_2CO_3 + 6\,NaNO_3 + 2\,CO_2$$

and which upon warming breaks down into yellow mercuric oxide and carbon dioxide.

$$Hg_3O_2CO_3 = 3\,HgO + CO_2$$

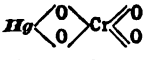
Mercuric chloride, $HgCl_2$, in solution, likewise reacts with soluble carbonates, but in such action the mercuric chloride tends to combine with precipitated mercuric oxide, giving rise to the insoluble mercuric oxychlorides already mentioned.

Hg=S When to a solution of mercuric nitrate, $Hg(NO_3)_2$, or other mercuric salt, is added either hydrogen sulphide, or some other soluble sulphide, a precipitate falls which is at first white, and consists of complex double compounds, such as $HgS \cdot Hg_2(NO_3)_2$, or $2\,HgS \cdot HgCl_2$, which turn yellow and brown, finally decomposing in the excess of the reagent, forming black *mercuric sulphide*, HgS.

$$Hg(NO_3)_2 + H_2S = \mathbf{HgS} + 2\,HNO_3$$

The black precipitate is acted upon by strong hydrochloric acid and by aqua regia, forming solutions. Nitric acid acts upon it to form the white insoluble double salt, $HgS \cdot Hg(NO_3)_2$.

Mercuric sulphide may also be made by rubbing mercury and sulphur together. It occurs native as the mineral *cinnabar*, one of the important mercury ores. It is used as a pigment.



From a solution of mercuric nitrate, $Hg(NO_3)_2$, or other mercuric salt, a soluble chromate such as potassium chromate, K_2CrO_4, will precipitate yellow *mercuric chromate*, $HgCrO_4$.

$$Hg(NO_3)_2 + K_2CrO_4 = \mathbf{HgCrO_4} + 2\,KNO_3$$

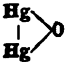
Hg=O *Mercuric oxide may also be formed as a precipitate.*

From a solution of mercuric nitrate, $Hg(NO_3)_2$, sodium hydroxide and other soluble hydroxides will precipitate yellow *mercuric oxide*, HgO.

$$Hg(NO_3)_2 + 2\,NaOH = \mathbf{HgO} + H_2O + 2\,NaNO_3$$

From solutions of mercuric chloride, which is relatively inert toward water, mercuric oxide may be precipitated by the action of alkali hydroxides in excess in hot solution, the reaction under other conditions, however, tending to the formation of insoluble mercuric oxychlorides. From solutions of mercuric cyanide, $Hg(CN)_2$, alkali hydroxides fail to precipitate mercuric oxide.

Mercurous Oxide.



Mercurous oxide may be formed as a precipitate by adding a soluble hydroxide to a mercurous salt in solution. When sodium hydroxide solution is added to a solution of mercurous nitrate, $Hg_2(NO_3)_2$, *mercurous oxide*, Hg_2O, falls as a black precipitate,

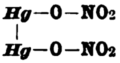
$$Hg_2(NO_3)_2 + 2\,NaOH = \mathbf{Hg_2O} + H_2O + 2\,NaNO_3$$

which, under the action of light, or when heated to 100°, decom into mercuric oxide and mercury.

$$Hg_2O = HgO + Hg$$

Mercurous Salts.

Some mercurous salts may be made by acting up excess of mercury or mercurous oxide with acids, o reducing the mercuric salts with mercury or other reducing agents. nearly all may be formed as precipitates.



$Hg-O-NO_2$, $Hg-O-NO_2$

Mercurous nitrate, $Hg_2(NO_3)_2$, may be obtained as anhydrous crystals by the action of dilute nitric ac the cold upon an excess of mercury.

$$6\,Hg + 8\,HNO_3 = 3\,Hg_2(NO_3)_2 + 4\,H_2O + 2\,NO$$

Mercurous nitrate does not dissolve completely in pure water. solutions of it may be made in water containing a little nitric ac combat the tendency to hydrolysis. The solution of mercurous n in water slightly acidulated with nitric acid becomes turbid dilution, because of the formation of insoluble oxynitrates, an prolonged action of water upon mercurous nitrate, a basic *curous hydroxynitrate*, $Hg_2(OH)NO_3$, may be obtained.

$$Hg_2(NO_3)_2 + H_2O = Hg_2(OH)NO_3 + HNO_3$$

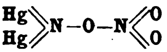
When mercurous nitrate is heated cautiously, nitrogen tetroxi evolved, while a residue is formed of mercuric oxide, which ma decomposed at higher temperatures.

$$Hg_2(NO_3)_2 = 2\,HgO + 2\,NO_2$$

When a solution of mercurous nitrate, containing nitric ac is allowed to stand, mercuric nitrate is gradually formed,

$$Hg_2(NO_3)_2 + 4\,HNO_3 = 2\,Hg(NO_3)_2 + 2\,H_2O + 2\,NO_2$$

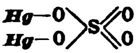
but such action of the nitric acid may be checked by keepin solution constantly in contact with mercury.



$Hg_2{>}N-O-N{<}O_2$

The action of ammonium hydroxide, NH upon mercurous nitrate, results in the pro of white insoluble *dimercurammonium nitrate,* NHg_2NO_3, blacke mercury in a state of fine division.

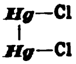
$$2\,Hg_2(NO_3)_2 + 4\,NH_4OH = \mathbf{NHg_2NO_3} + \mathbf{2\,Hg} + 3\,NH_4NO_3 + 4$$



Mercurous sulphate, Hg_2SO_4, may be formed by heating an excess of mercury with concentrated sulphuric acid, sulphur dioxide being evolved.

$$2\,Hg + 2\,H_2SO_4 = Hg_2SO_4 + 2\,H_2O + SO_2$$

Mercurous sulphate is also formed as a sparingly soluble precipitate by adding sulphuric acid to a solution of mercurous nitrate, $Hg_2(NO_3)_2$.



$$\begin{array}{l} Hg-Cl \\ \mid \\ Hg-Cl \end{array}$$

Mercurous chloride, Hg_2Cl_2 (calomel), may be produced in association with mercuric chloride when chlorine and mercury combine in suitable proportions.

$$2\,Hg + Cl_2 = Hg_2Cl_2$$

It is more conveniently obtained by reactions in which mercuric chloride suffers reduction, or by precipitation from solutions of mercurous nitrate.

When mercuric chloride, $HgCl_2$, is heated over mercury, mercurous chloride, Hg_2Cl_2, results.

$$HgCl_2 + Hg = Hg_2Cl_2$$

A similar process, in which mercuric sulphate, $HgSO_4$, sodium chloride, NaCl, and mercury are heated in mixture, producing mercurous chloride as a sublimate, is employed for the commercial preparation of mercurous chloride.

Stannous chloride, $SnCl_2$, reduces mercuric chloride, $HgCl_2$, in solution, forming mercurous chloride,

$$2\,HgCl_2 + SnCl_2 = \mathbf{Hg_2Cl_2} + SnCl_4$$

and then acts upon the mercurous chloride with separation of mercury.

$$Hg_2Cl_2 + SnCl_2 = 2\,\mathbf{Hg} + SnCl_4$$

Sulphurous acid, H_2SO_3, in water solution, reduces mercuric chloride to mercurous chloride,

$$2\,HgCl_2 + H_2SO_3 + H_2O = \mathbf{Hg_2Cl_2} + H_2SO_4 + 2\,HCl$$

and in hot solution acts further upon the mercurous chloride with separation of mercury.

$$Hg_2Cl_2 + H_2SO_3 + H_2O = 2\,\mathbf{Hg} + H_2SO_4 + 2\,HCl$$

When hydrochloric acid, sodium chloride, or any other soluble chloride is added to a solution of mercurous nitrate, $Hg_2(NO_3)_2$, *mercurous chloride*, Hg_2Cl_2, is formed as a white precipitate.

$$Hg_2(NO_3)_2 + 2\,HCl = Hg_2Cl_2 + 2\,HNO_3$$

Mercurous chloride, crystalline when formed by sublimation, amorphous or partly crystalline when precipitated, is a white solid, of specific gravity 7.2, insoluble in water and in alcohol. It is largely used as a medicine.

Mercurous chloride volatilizes at red heat, with consequent dissociation, forming a colorless vapor containing mercuric chloride and mercury, which upon cooling recombine to form a sublimate of mercuric chloride.

$$Hg_2Cl_2 \rightleftarrows HgCl_2 + Hg$$

Sunlight changes mercurous chloride gradually into mercuric chloride and mercury, and a similar decomposition of mercurous chloride may be brought about by heating it with hydrochloric acid or with concentrated solutions of chlorides.

It has been shown that certain reducing agents, such as stannous chloride, $SnCl_2$, and sulphurous acid, H_2SO_3, may act upon mercurous chloride, Hg_2Cl_2, to separate mercury. Oxidizing agents, on the other hand, tend to change mercurous chloride into mercuric chloride or other mercuric salts. Chlorine in the presence of water changes mercurous chloride, Hg_2Cl_2, to mercuric chloride, $HgCl_2$.

$$Hg_2Cl_2 + Cl_2 = 2\,HgCl_2$$

Nitric acid acts upon mercurous chloride, Hg_2Cl_2, to form mercuric chloride, with more or less mercuric nitrate, $Hg(NO_3)_2$, and nitrogen oxides,

$$3\,Hg_2Cl_2 + 8\,HNO_3 = 3\,HgCl_2 + 3\,Hg(NO_3)_2 + 4\,H_2O + 2\,NO$$

and the action of aqua regia is similar.

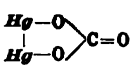
$$3\,Hg_2Cl_2 + 2\,HNO_3 + 6\,HCl = 6\,HgCl_2 + 4\,H_2O + 2\,NO$$

When ammonium hydroxide, NH_4OH, acts upon mercurous chloride, Hg_2Cl_2, the result is a mixture of the double salt of *dimercurammonium chloride* and ammonium chloride and finely divided mercury, which imparts to the mixture a black color.

$$2\,Hg_2Cl_2 + 4\,NH_4OH = NHg_2Cl \cdot NH_4Cl + 2\,Hg + 2\,NH_4Cl + 4\,H_2O$$

Mercurous bromide, Hg_2Br_2, is a white precipitate formed by acting upon a solution of a mercurous salt with a soluble bromide, or by subliming a mixture of mercury and mercuric bromide.

Mercurous iodide, Hg_2I_2, is a green powder formed by rubbing together iodine and an excess of mercury with alcohol, or by precipitation by potassium iodide from a solution of mercurous nitrate. An excess of alkali iodide tends to decompose it into mercuric iodide and mercury.



When sodium carbonate, Na_2CO_3, is added to a solution of mercurous nitrate, $Hg_2(NO_3)_2$, a yellow precipitate of a *mercurous carbonate*, contaminated with a basic mercurous nitrate, is formed. After standing for several days in contact with an excess of sodium carbonate, and frequent shaking, the composition of the quickly washed precipitate is nearly that of the neutral carbonate, Hg_2CO_3.

$$Hg_2(NO_3)_2 + Na_2CO_3 = \mathbf{Hg_2CO_3} + 2\,NaNO_3$$

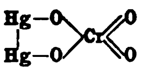
The precipitate tends to decompose slowly, and at 130° is resolved into mercury, mercuric oxide, and carbon dioxide.

$$Hg_2CO_3 = Hg + HgO + CO_2$$

$Hg{=}S$

Hydrogen sulphide, H_2S, and other soluble sulphides produce in a solution of mercurous nitrate, $Hg_2(NO_3)_2$, a black precipitate of *mercuric sulphide*, HgS, and mercury.

$$Hg_2(NO_3)_2 + H_2S = \mathbf{HgS} + Hg + 2\,HNO_3$$



From a solution of mercurous nitrate, $Hg_2(NO_3)_2$, a soluble chromate, such as potassium chromate, K_2CrO_4, precipitates a bright red precipitate of a basic *mercurous chromate*, approximating to the symbol $Hg_8Cr_3O_{13}$.

$$4\,Hg_2(NO_3)_2 + 3\,K_2CrO_4 = \mathbf{Hg_8Cr_3O_{13}} + 6\,KNO_3 + 2\,KNO_3$$

Upon boiling this precipitate with suitably dilute nitric acid, mercurous nitrate, $Hg_2(NO_3)_2$, is formed, and neutral mercurous chromate, Hg_2CrO_4, remains as a crystalline powder. Strong nitric acid decomposes neutral mercurous chromate.

Dimercurammonium Derivatives. *By the action of ammonia or of ammonium hydroxide upon mercuric or mercurous compounds, the dimercurammonium derivatives may be obtained.*

By the action upon mercuric oxide, HgO, of dilute ammonium hydroxide, a pale yellow powder having the composition $NHg_2OH \cdot 2\,H_2O$ may be obtained which when heated to 80°–85° forms anhydrous *dimercurammonium hydroxide*, NHg_2OH, as a pale brown explosive powder.

$$2\,HgO + NH_4OH = NHg_2OH + 2\,H_2O$$

This, when heated to 100°, yields *dimercurammonium oxide*, $(NHg_2)_2O$, as a dark brown explosive powder.

$$2(NHg_2)OH = (NHg_2)_2O + H_2O$$

The corresponding *dimercurammonium salts*, such as the double salts of *dimercurammonium chloride* with ammonium chloride, $NHg_2Cl \cdot NH_4Cl$ (infusible white precipitate), and $NHg_2Cl \cdot 3\,NH_4Cl$ (fusible white precipitate), and the *dimercurammonium nitrate*, NHg_2NO_3, have been mentioned in connection with the respective mercuric and mercurous salts, from which they may be formed by addition of ammonium hydroxide.

Decomposition of Mercury Compounds

The mercury compounds may all be decomposed by heating them strongly in dry condition in intimate mixture with dry sodium carbonate. When, for example, an intimate mixture of mercuric chloride, $HgCl_2$, and sodium carbonate, both in dry condition, is heated strongly in a glass tube closed at one end, mercury is vaporized and sublimes as a gray "mirror" on the further wall of the tube; and a similar sublimate may be formed by heating other mercury compounds with sodium carbonate.

$$2\,HgCl_2 + 2\,Na_2CO_3 = 2\,Hg + 4\,NaCl + 2\,CO_2 + O_2$$

Replacement of Mercury in Salts.

Most of the common metals, being electro-positive to mercury, will replace mercury in solutions of its salts.

A strip of zinc or of cadmium immersed in a solution of mercuric chloride, $HgCl_2$, of sufficient concentration, will speedily become covered with a dark coating of finely divided mercury, which when burnished will assume the characteristic bright luster of ordinary mercury.

$$HgCl_2 + Zn = ZnCl_2 + \mathbf{Hg}$$
$$HgCl_2 + Cd = CdCl_2 + \mathbf{Hg}$$

Similarly, the more electro-positive magnesium, aluminium, lead, tin, and iron may spontaneously replace mercury from suitable solutions of its salts, while mercury will itself replace from their salt solutions the more electro-negative silver, gold, and platinum.

Summary. *Mercuric oxide may be formed by heating mercury in air, and by heating certain mercury salts, and may be decomposed by heating into oxygen and mercury.*

Mercuric nitrate, formed by the action of an excess of nitric acid upon mercury, may be decomposed by action of water, forming an oxynitrate or mercuric oxide; may be decomposed by heating, forming mercuric oxide or mercury; and may be reduced to mercurous nitrate by the action of mercury. Mercuric sulphate may be formed by heating mercury with an excess of sulphuric acid. Mercuric chloride may be made by the combination of mercury with chlorine, by the action of hydrochloric acid upon mercuric oxide, by heating an alkali chloride with mercuric sulphate; it forms double compounds with mercuric oxide, and with chlorides and other salts; it may be reduced to mercurous chloride, and even to metallic mercury, by the action of mercury, stannous chloride, or sulphurous acid. Mercuric bromide and mercuric iodide may be made by direct union of their elements, and in other ways. Mercuric oxycarbonate, mercuric sulphide, mercuric chromate, and mercuric oxide may be precipitated from solutions of mercuric salts by suitable reagents.

Mercurous oxide may be precipitated from mercurous nitrate solution by alkali hydroxides, and upon heating decomposes into mercuric oxide and mercury.

Mercurous nitrate, formed by the action of nitric acid upon an excess of mercury, may be decomposed by water with formation of a basic nitrate, may be decomposed by heating with formation of mercuric oxide or mercury, and may be oxidized by nitric acid to form mercuric nitrate. Mercurous sulphate may be formed by heating an excess of mercury with sulphuric acid, or by adding sulphuric acid to a solution of a mercurous salt. Mercurous chloride may be formed by combination of mercury with chlorine, by the reduction of mercuric chloride by mercury, stannous chloride, or sulphurous acid, or by the action of soluble chlorides upon solutions of mercurous salts; it may be oxidized by nitric acid and aqua regia to form mercuric chloride; it may be reduced to mercury by stannous chloride or sulphurous acid. Mercurous bromide and mercurous *iodide may be made by combination of their elements and in other ways. Mercurous carbonate and mercurous oxide may be precipitated from solutions of mercurous salts.*

By the action of ammonia or ammonium hydroxide upon mercuric oxide, dimercurammonium hydroxide is formed, which, on heating, decomposes into dimercurammonium oxide and water. Similarly constituted dimercurammonium salts may be formed by the action of ammonium hydroxide upon mercuric salts, and also upon mercurous salts, their formation in the latter case being accompanied by the separation of mercury in fine division.

All mercury compounds yield mercury when heated with sodium carbonate in dry condition. Zinc, cadmium, and other more positive elements will replace mercury from solutions of its salts; while other more negative elements may be replaced by mercury.

CHAPTER XIII

SECONDARY SERIES—GROUP III

GALLIUM, Ga, 70
INDIUM, In, 115
THALLIUM, Tl, 204.1

THE three elements of Group III of the primary series are represented by exceedingly small quantities of their compounds in certain rare minerals, and occur as impurities in zinc blendes and in other common ores, in which they may be detected by means of the characteristic lines which they give in the spectroscope. Gallium is found not only in zinc ores, but also in many ores of iron, aluminium, and manganese; indium is also present in ores of zinc, iron, manganese, and tin; while thallium occurs in ores of zinc, copper, and iron, and has been noted as a constituent of certain mineral waters containing also rare alkali salts. Compounds of these elements sometimes occur in the flue dust from furnaces in which pyrite has been roasted. The three elements of the group exhibit characteristic line spectra when vaporized before the spectroscope. Gallium chloride gives a spark spectrum of two violet lines. Indium salts give a flame spectrum of one intense indigo blue line, and one violet line, and impart a violet color to flame.

It was by means of the spectroscope that all three of these rare elements were discovered: gallium by Lecoq de Boisbaudran, in 1875, in a zinc blende from the Pyrenees; indium, by Reich and Richter, in 1863; and thallium by Crookes, in 1861, both from ores in the Hartz Mountains. The existence of gallium had been predicted by Mendeléeff in 1869 from the relations disclosed by the periodic system, and the properties of the element, called by Mendeléeff *eka-aluminium*, were foretold.

Gallium, indium, and thallium, and their oxides and hydroxides as well, are generally acted upon by strong acids with formation of salts in which these elements are electro-positive. We therefore recognize the hydroxides of these elements as weak bases, and the elements and their oxides as base-forming elements and oxides. Gallium hydroxide and indium hydroxide may also interact with strong basic hydroxides, but the thallium hydroxide shows no tendency to form salts in which the element is electro-negative. All three elements show more than one valence.

The three elements themselves, moderately heavy metals, similar to one another in most properties, and possessed of specific gravities and melting points which vary in the order of their atomic weights, are extracted from their ores by special processes involving the careful separation of elements.

Gallium is best obtained directly from certain *zinc blendes*, the minerals in which it most commonly occurs. The gallium-bearing mineral is treated with aqua regia, and to the cold solution, freed from the excess of acid by boiling, zinc is added to precipitate compounds of many other elements associated with the gallium in the mineral. The filtrate from the compounds thus precipitated throws down upon long boiling with zinc a basic salt of gallium, associated with salts of aluminium, iron, and zinc. The impure basic salt of gallium is treated with hydrochloric acid, to the resulting solution hydrogen sulphide is added, the excess of this reagent is boiled out, and sodium carbonate is added fractionally so long as the test of the solution by the spark spectrum shows the two violet lines characteristic of gallium compounds. The successive precipitates are united and treated with sulphuric acid, and from the resulting solution, largely diluted, basic gallium sulphate is precipitated by boiling, filtered off, and again treated with sulphuric acid. Potassium hydroxide in excess is now added, and after the separation of ferric hydroxide, carbon dioxide precipitates gallium hydroxide, which forms with potassium hydroxide a solution from which gallium may be obtained by electrolysis.

Gallium, a lustrous gray metal of specific gravity 5.9, melting at 30°, oxidizing superficially when heated to high temperatures in the air, is acted upon by hydrochloric acid and by warm nitric acid, and by strong basic hydroxides. Among the characteristic *gallium compounds* in which gallium is generally trivalent but sometimes divalent, may be mentioned *gallium sulphate*, $Ga_2(SO_4)_3$; *gallium nitrate*, $Ga(NO_3)_3$, formed by the action upon gallium residues of sulphuric acid and nitric acid respectively; the *gallium chlorides*, $GaCl_2$ and $GaCl_3$, formed by the action of chlorine or hydrochloric acid upon gallium; *gallium hydroxide*, $(GaOH)_3$, formed as a precipitate by the action of soluble hydroxides upon solutions of gallium salts; *gallium trioxide*, Ga_2O_3, formed by heating the nitrate or the hydroxide; and *gallium monoxide*, GaO, said to be formed by reducing gallium trioxide. Gallium sulphate forms with ammonium sulphate a double compound, $NH_4Ga(SO_4)_2 \cdot 12\ H_2O$, which may be classed with the *alums*. The gallium compounds are to some extent hydrolyzed in dilute solutions, forming insoluble basic compounds.

In extracting *indium* from certain *zinc blendes* it is best to proceed with the reduction of the zinc by the usual metallurgical processes, and then to treat the crude zinc to get the indium. When the reduced zinc is nearly all acted upon by the hydrochloric acid or nitric acid, the indium remains in the residue of zinc still unacted upon, with many impurities. This residue, after washing with water and dilute sulphuric acid, is treated with nitric acid, and the solution is evaporated with sulphuric acid until the nitric acid is expelled, and diluted to allow the lead compound to precipitate. From the remaining solutions a precipitate of indium hydroxide, contaminated with ferric hydroxide, is obtained by the action of ammonium hydroxide, and this precipitate is treated with hydrochloric acid, forming a solution which when boiled with an excess of sodium sulphite deposits basic indium sulphite. This basic salt upon ignition yields indium oxide, and this, when reduced by hydrogen or sodium, yields indium.

Indium is a soft white metal, of specific gravity 7.42, melting at 176°, burning readily with a violet flame when strongly heated, acted upon by hydrochloric acid, nitric acid, and sulphuric acid. The *indium compounds* are for the most part analogous in their composition and modes of formation to the corresponding compounds of gallium. In them indium is generally trivalent, although in certain compounds it is divalent or univalent. Among the indium compounds are *indium sulphate*, $In_2(SO_4)_3$; *indium nitrate*, $2\,In(NO_3)_3 \cdot 9\,H_2O$; the *indium chlorides*, $InCl_3$, $InCl_2$, and $InCl$; *indium hydroxide*, $In(OH)_3$; the *indium oxides*, In_2O_3, and InO; and the *alums*, $KIn(SO_4)_2 \cdot 12\,H_2O$, and $NH_4In(SO_4)_2 \cdot 12\,H_2O$. In addition to these we may note *indium sulphide*, In_2S_3, precipitated by the addition of hydrogen sulphide to solutions of indium salts, and acted upon by soluble sulphides to form sulphosalts, such as $KInS_2$.

From the minerals containing *thallium* the element is prepared by treating with aqua regia, evaporating after addition of sulphuric acid until the free acid is removed, diluting, neutralizing with sodium carbonate, and adding potassium cyanide. Lead and bismuth compounds are thus precipitated, leaving a solution from which thallium sulphide may be precipitated, possibly in company with cadmium sulphide and mercury sulphide. From the thallous sulphide by action of sulphuric acid thallous sulphate is formed, from which the metal may be deposited by the action of zinc or the electric current. When *flue dust* is the original material, it is boiled with water, and from the resulting solution thallous chloride is precipitated by hydrochloric acid. The crude thallous chloride thus obtained may be purified by a process of treatment involving the addition of sulphuric acid, heating until all hydrochloric acid and the greater part of the sulphuric acid is expelled, dilution with water, precipitation of insoluble compounds from the solution by calcium carbonate, filtration, and final precipitation by hydrochloric acid. From the thallous chloride the thallium may be got by fusion with sodium carbonate and potassium cyanide; or the chloride may be changed into the sulphate, the water solution of which may be acted upon by zinc or electrolyzed.

Thallium is a whitish or gray metal, with dull luster, soft and malleable, of specific gravity 11.8, melting at 290°, oxidizing readily at high temperatures, and at ordinary temperature in moist air. It is acted upon by sulphuric acid and nitric acid, but hydrochloric acid acts only superficially, forming the insoluble thallous chloride. There are two well-defined series of *thallium compounds*, in one of which it is univalent, while in the others it is trivalent. The compounds of the element in its lower condition of valence are ordinarily the more stable. When thallium is burned in oxygen, *thallium trioxide*, Tl_2O_3, is formed, which at red heat loses oxygen and becomes *thallium monoxide*, TlO. The monoxide, formed also by the action of air upon thallium at ordinary temperature, combines with water to form *thallous hydroxide*, $Tl(OH)_2$.

Of the *thallous salts* which correspond in composition to thallium monoxide and thallous hydroxide we note the *sulphates*, Tl_2SO_4, and $TlHSO_4$, formed by the action of sulphuric acid upon thallium or thallous oxide; *thallium nitrate*, $TlNO_3$, formed by the action of nitric acid upon thallium; *thallium chloride*, TlCl, formed when thallium burns in chlorine, or when hydrochloric acid acts upon a thallous salt; and *thallium sulphide*, Tl_2S, precipitated by hydrogen sulphide from solutions of thallous salts. Several *alums*, such as $TlAl(SO_4)_2 \cdot 12\ H_2O$, are known, as is also the insoluble *thallium chlorplatinate*, Tl_2PtCl_6.

Of the *thallic salts*, corresponding to thallium trioxide, Tl_2O_3, and *thallic hydroxide*, $Tl(OH)_3$, which when dried has the composition (TlO)OH, we may mention *thallium sulphate*, $Tl_2(SO_4)_3$, and *thallium nitrate*, $Tl(NO_3)_3 \cdot 4\ H_2O$, formed by acting upon thallium trioxide with sulphuric acid and nitric acid respectively; *thallium chloride*, TCl_3, formed by the action of chlorine upon thallous chloride; and *thallium sulphide*, Tl_2S_3, formed by heating thallium with sulphur. The thallic salts are unstable and may be acted upon by water with precipitation of oxy-compounds. Thallous compounds may be oxidized to thallic compounds by oxidizing agents, and the thallic compounds may be reduced to thallous compounds by reducing agents.

CHAPTER XIV

SECONDARY SERIES — GROUP IV

GERMANIUM, Ge, 72.5
Tin, Sn, 119.0
Lead, Pb, 206.9

Group IV. THE elements of Group IV of the secondary series, germanium, tin, and lead, are gray or white lustrous metals, fusible and volatile at high temperatures, malleable, having high specific gravities which increase as the atomic weights increase. All three elements are practically unaffected by air or water. Tin and lead may be melted and cast in molds, and will combine readily with other metals to form useful alloys. Germanium is a rare element, being found only in small proportions in a few rare minerals; while tin and lead are found widely distributed in the earth as constituents of a few important minerals, from which, since very early times, these elements have been obtained for commercial purposes.

Germanium was discovered in 1886 by Winkler, in the rare mineral *argyrodite*, $4\,Ag_2S \cdot GeS_2$, from which by suitable treatment the element may be prepared.

Chemical Relations. Germanium, tin, and lead, although usually electro-positive, in their formation of salts are both base-forming and acid-forming. Both tin and lead, and their oxides and hydroxides, are attacked by strong acids and by strong bases, the strong acids forming well-characterized salts, such as sulphates and nitrates, in which tin and lead are positive ions; while the strong bases form compounds, such as well-known *stannates* and certain *plumbates*, in which these elements are in the negative ions. Germanium shows similar basic and acidic relations in its compounds. All three elements of the group form chlorides, sulphides, and similar binary compounds by direct combination of the elements.

Salts. Each of the three elements of the group forms two or more oxides. Tin forms two classes of salts, the *stannic salts* and the *stannous salts*, corresponding respectively to its two oxides and differing from one another in the proportions in which tin enters into their composition. Two similar classes of germanium salts are known, while the more common lead salts correspond to the lower lead oxide. The compounds of germanium, tin, and lead are generally stable, many of them being insoluble; a few are hydrolyzed by water. Since the salts of these elements are not generally volatile, their composition is for the most part represented by symbols similar to those of known volatile compounds, in which the prevailing valence of these elements is IV or II.

Tin Ore. Tin occurs principally in the mineral *cassiterite*, SnO (tin stone), which is found disseminated or in masses in granite rocks, or in gravels formed by the disintegration of granite by running water. In some regions the tin ores or gravels also contain gold, while in other places the tin is associated with the minerals of copper, zinc, and lead. In the United States the deposits of tin ores have not been found sufficient to pay for mining them extensively. The world's chief supply of tin now comes from the Malay Peninsula and from Cornwall, in England, the latter mines being the oldest and most extensive in the world. Tin is also mined in Germany and Austria.

Lead Ores. Small amounts of lead are found free in volcanic rocks and in certain ores, and traces of lead are present in sea water and in sea plants. The world's supply of lead, however, is obtained from ores in which the lead minerals are associated with those of zinc, and frequently with silver and gold. The most important lead minerals are the gray lustrous *galenite*, PbS (galena), found usually in deep ores which have never been exposed, and the lighter colored *cerussite*, $PbCO_3$, and *anglesite*, $PbSO_4$, found often in surface ores which have been weathered. *Pyromorphite*, $3\,Pb_3(PO_4)_2 \cdot PbCl_2$, colored more or less by impurities, occurs in many localities. The argentiferous, or silver-containing, lead ores are usually found in the older stratified rocks, as in the Cordilleras in the United States, while the non-argentiferous ores occur in the stratified rocks, such as the limestones of Missouri. The more important lead mines of the United States are those of Colorado, Utah, and Idaho.

Tin and lead are reduced from their ores by simple metallurgical processes, the former by reduction of the oxide by carbon, and the latter similarly or by regulated washing of the sulphide in air. Both of these metals, because of their stability in air and water, and their malleability, are useful in pure condition and in alloys.

GERMANIUM, Ge, 72.5

Germanium was discovered by Winkler in 1886, and fills in the periodic scheme the vacancy for which Mendeléeff predicted that an element which he named *eka-silicon* would be found. It is found chiefly in the very rare mineral *argyrodite*, $4\,Ag_2S \cdot GeS_2$, and is likewise present in small amounts in some other rare minerals. When heated to redness in hydrogen, argyrodite yields a sublimate of impure *germanous sulphide*, GeS, which, when purified by acting upon it with ammonium sulphide and reprecipitating it with hydrochloric acid, may be converted to *germanium dioxide*, GeO_2, by treatment with nitric acid and evaporation of this mixture to dryness. By heating germanium dioxide in a current of hydrogen, germanium may be obtained.

Germanium is a grayish white metal, of specific gravity 5.469, melting at 900°, volatilizing somewhat in hydrogen at 1350°, unaffected by the air at ordinary temperatures, oxidizing in air at red heat to germanium dioxide, GeO_2, not attacked by hydrochloric acid, converted by nitric acid to a hydrated derivative of germanium dioxide, GeO_2. Germanium forms two series of compounds, in one of which it appears as a bivalent positive ion, while in the other it is quadrivalent, and positive or negative according to its association.

Representative of *germanous compounds* are *germanous chloride*, $GeCl_2$, obtained in impure anhydrous condition by the action of hydrogen chloride upon heated germanous sulphide, and in solution by action of concentrated hydrochloric acid upon germanous sulphide; yellow *germanous hydroxide*, $Ge(OH)_2$, obtained when germanous chloride in solution is acted upon by an alkali hydroxide; steel-gray *germanous oxide*, GeO, formed by heating germanous hydroxide; and *germanous sulphide*, GeS, obtained as a reddish brown precipitate by the action of hydrogen sulphide upon the solution of germanous chloride, or as gray-black crystals when sublimed in hydrogen.

Representative *germanic compounds* are *germanic chloride*, $GeCl_4$, in which germanium is the positive ion, a colorless fuming liquid at 86°, hydrolyzed by water, and of vapor density corresponding to the symbol; *germanic hydroxide*, $Ge(OH)_4$, or a derivative by dehydration, produced by hydrolysis of germanic chloride, nearly insoluble, generally acidic in character, being easily attacked by alkali hydroxides in solution and by alkali carbonates in fusion; white, slightly soluble *germanium dioxide*, GeO_2, produced by heating germanic hydroxide, by roasting the metal in air, or by treating the metal with nitric acid and heating the residue; *germanic sulphide*, GeS_2, white and voluminous, formed when solutions of germanic sulphosalts, made by fusion of germanium compounds with sulphur and alkali carbonates, are acidulated.

Tin, Sn, 119.0

Reduction of Tin Ore. When *cassiterite*, SnO_2, is strongly heated with carbon under suitable conditions, a residue of tin is produced, carbon dioxide escaping.

$$SnO_2 + C = Sn + CO_2$$

In the *metallurgy of tin*, the tin ores, consisting of *cassiterite* together with oxides, arsenides, and sulphides of other elements, are first roasted to remove sulphur and arsenic, and are then heated with carbon in a furnace from which the molten tin is drawn off and cast into bars, which may be further purified by remelting, the pure tin being allowed to run away from the residues of other metals.

Properties of Tin. *Tin* is a white metal of fine crystalline structure, of specific gravity 7.3, ordinarily soft and malleable and very ductile, but at 200° becoming brittle, while at 231° it melts, and at red heat forms a vapor. By etching the surface of tin, its crystalline structure is revealed by the appearance of striations, while when a bar of tin is bent, a peculiar crackling sound (tin cry) is produced, which may be due to the friction of the crystals upon one another. Tin, when exposed to low temperatures, or when undisturbed for a long time, changes spontaneously into *gray tin*, a grayish powder of specific gravity 5.8. Tin which has been rolled into very thin sheets is known as *tin foil.*

Tin is not acted upon by air or water at ordinary temperatures. When heated in air above its melting point, it becomes covered with a white film of stannic oxide, and at white heat it burns with a brilliant white light, forming white clouds of oxide. Tin is not acted upon by water at ordinary temperatures, but at red heat tin decomposes steam with evolution of hydrogen. Hydrochloric acid acts upon tin with evolution of hydrogen and the formation of stannous chloride, while strong sulphuric acid forms stannous sulphate with sulphur dioxide and sulphur. Dilute nitric acid acts upon tin to form a tin nitrate, while concentrated nitric acid forms stannic nitrate or stannic hydroxide. Tin is attacked by strongly basic hydroxides, with formation of salts, and at high temperatures with evolution of hydrogen. Tin forms alloys with antimony, bismuth, copper, mercury, lead, and other metals, and combines directly with sulphur, chlorine, and other negative elements.

Uses of Tin.

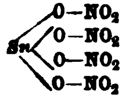
On account of the difficulty with which it is attacked by other substances, tin is used as a protective covering on other metals, as in the case of the common *tin plate*, made by dipping sheet iron into molten tin. The most important tin alloys are the *soft solders* and the *pewters*, containing tin and lead in varying proportions; *Britannia metal*, consisting of tin and antimony together with small amounts of other elements; *fusible metals*, consisting of tin, bismuth, and sometimes lead and cadmium. The bronzes and the amalgams of tin have been mentioned under copper and mercury respectively.

Oxides and Salts.

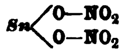
Tin forms two oxides: *stannic oxide*, SnO_2, and *stannous oxide*, SnO. Corresponding to stannic oxide, we have a few unstable *stannic salts* and the more stable *stannic hydroxides*, which act like weak acids in forming *stannates*, salts in which tin is negative. Corresponding to stannous oxide we have similarly *stannous salts*, weakly acidic *stannous hydroxides*, and *stannites*.

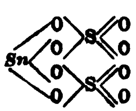
Stannic and Stannous Salts.

We shall study first the stannic salts and stannous salts, in which tin plays the part of the positive ion, and which may be formed by acting upon tin with suitable reagents.

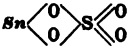


When tin is acted upon by dilute nitric acid of suitable strength, *stannic nitrate*, $Sn(NO_3)_4$, is formed as a white powder, soluble in water, and easily hydrolyzed, with formation of a stannic hydroxide, the composition of which depends upon the conditions. If sufficiently dilute nitric acid acts upon tin, the readily hydrolyzed *stannous nitrate*, $Sn(NO_3)_2$, may be formed. In either case ammonium nitrate may be formed along with the stannic nitrate or the stannous nitrate.

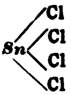




By the action upon tin of hot concentrated sulphuric acid, *stannic sulphate*, $Sn(SO_4)_2$, may be formed, which may be obtained from the solution in the crystallized form $Sn(SO_4)_2 \cdot 2\,H_2O$ and as the oxysalt, $Sn_2O_2(SO_4)_2 \cdot 2\,H_2O$, both of which are hydrolyzed by water. The formation of stannic sulphate is accompanied by formation of sulphur dioxide and sulphur. Stannic sulphate may also be formed as precipitate by adding sulphuric acid to a dilute solution of stannic chloride.



When sulphuric acid of suitable dilution acts upon tin, the readily hydrolyzed *stannous sulphate*, $SnSO_4$, is formed, hydrogen being evolved.

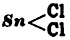


When chlorine is passed into molten tin, heat and light are evolved, and *stannic chloride*, $SnCl_4$, is formed as a colorless, strongly fuming liquid of specific gravity 2.27, solidifying at −33° and boiling at 114°, forming a vapor of specific gravity corresponding to the symbol given.

$$Sn + 2\,Cl_2 = SnCl_4$$

Stannic chloride attracts water from the air, forming a crystalline hydrate, $SnCl_4 \cdot 3\,H_2O$, soluble in water. From the water solution of stannic chloride this hydrate, as well as those having the composition $SnCl_4 \cdot 5\,H_2O$ and $SnCl_4 \cdot 8\,H_2O$, may be crystallized, while on boiling the solution, or on allowing very dilute solution to stand, stannic hydroxides are precipitated.

Stannic chloride combines with hydrochloric acid, with formation of $SnCl_4 \cdot 2\,HCl \cdot 6\,H_2O$ which may be regarded as *chlorstannic acid* $H_2SnCl_6 \cdot 6\,H_2O$. Stannic chloride combines with other chlorides to form such compounds as $SnCl_4 \cdot 2\,KCl$ or K_2SnCl_6, which may be regarded as *chlorstannates*. The compound $SnCl_4 \cdot 2\,NH_4Cl$, or $(NH_4)_2SnCl_6$, is the so-called "pink salt" used as a mordant in dyeing. Other double salts, such as $SnCl_4 \cdot PCl_5$ and $SnCl_4 \cdot 2\,SCl_4$, are also formed.



When tin is heated in dry hydrochloric acid gas, white crystalline *stannous chloride*, $SnCl_2$, is formed, which is soluble in water, and melts at 250°. At 606° stannous chloride forms a vapor which at 900° has the specific gravity corresponding to the molecular symbol given. At a lower temperature the molecule Sn_2Cl_4 appears likewise to exist.

$$Sn + 2\,HCl = SnCl_2 + H_2$$

By the action of concentrated hydrochloric acid upon tin, a solution is formed from which may be obtained crystals of the composition $SnCl_2 \cdot 2\,H_2O$. This hydrate is the "tin salt" used as a mordant.

When the dilute solution of stannous chloride is allowed to stand it becomes turbid on account of the formation of the insoluble basic salt, Sn(OH)Cl, and the same salt may be formed along with stannic chloride when stannous chloride solution remains in contact with air.

When crystallized stannous chloride is heated, stannous oxide, SnO, and hydrochloric acid are formed.

$$SnCl_2 + H_2O = SnO + 2\ HCl$$

Stannous chloride combines with many other chlorides to form double chlorides such as $SnCl_2 \cdot 2\ KCl$ and $2\ NH_4Cl \cdot SnCl_2$.

Stannous chloride combines readily with free chlorine to form stannic chloride, $SnCl_4$,

$$SnCl_2 + Cl_2 = SnCl_4$$

and it will remove the chlorine from many other chlorides, such as mercuric chloride, $HgCl_2$, in water solution, and is therefore useful as a reducing agent.

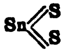
$$2\ HgCl_2 + SnCl_2 = SnCl_4 + \mathbf{Hg_2Cl_2}$$
$$HgCl_2 + SnCl_2 = SnCl_4 + \mathbf{Hg}$$

Stannous chloride is formed in solution from stannic chloride by the action of nascent hydrogen or of certain metals.

$$SnCl_4 + H_2 = SnCl_2 + 2\ HCl$$
$$SnCl_4 + Mg = SnCl_2 + MgCl_2$$

Similar to the chlorides of tin we have *fluorides*, *bromides*, and *iodides*, and double fluorides of tin and other elements, such as $SnF_4 \cdot 2\ KF$, or K_2SnF_6, known as *fluostannates*.

Tin Sulphides. *The sulphides of tin may be formed as precipitates by acting upon solutions of tin salts with soluble sulphides.*



When to a solution of stannic chloride, $SnCl_4$, hydrogen sulphide is added, a precipitate of yellow *stannic sulphide*, SnS_2, is obtained, which may be acted upon by concentrated hydrochloric acid.

$$SnCl_4 + 2\ H_2S = \mathbf{SnS_2} + 4\ HCl$$

Ammonium sulphide, $(NH_4)_2S$, added in proper amount, precipitates stannic sulphide from solutions of stannic salts,

$$SnCl_4 + 2\ (NH_4)_2S = \mathbf{SnS_2} + 4\ NH_4Cl$$

and the precipitate is acted upon by an excess of the reagent with formation of soluble *ammonium sulphostannate*, $(NH_4)_2SnS_3$.

$$SnS_2 + (NH_4)_2S = (NH_4)_2SnS_3$$

Acids will act upon this solution with formation of hydrogen sulphide and precipitation of stannic sulphide. Sodium sulphide, Na_2S, and potassium sulphide, K_2S, will similarly act upon stannic sulphide to form sulphostannates.

Stannic sulphide, SnS_2 (tin disulphide), when precipitated, is an amorphous yellow powder. It may be formed as a bright yellow crystalline mass by heating a mixture of finely divided tin, sulphur, and ammonium chloride, and when thus prepared is used in bronzing under the name "mosaic gold." By the action of ammonium sulphide or alkali sulphides upon stannic sulphide *sulphostannates* may be formed. *Sodium sulphostannate* forms crystals of the composition $Na_2SnS_3 \cdot 2H_2O$. The sulphostannates are acted upon by acids, with precipitation of stannic sulphide and evolution of hydrogen sulphide.

$Sn = S$

When hydrogen sulphide, H_2S, or ammonium sulphide, $(NH_4)_2S$, is added to a solution of stannous chloride, $SnCl_2$, a precipitate is obtained of dark brown *stannous sulphide*, SnS, which may be acted upon by concentrated hydrochloric acid.

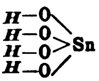
$$SnCl_2 + H_2S = \mathbf{SnS} + 2\ HCl$$

Stannous sulphide is not acted upon by ammonium sulphide alone, but in the presence of free sulphur ammonium sulphide converts it into soluble *ammonium sulphostannate*, $(NH_4)_2SnS_3$, which is acted upon by acids in the manner shown. Sodium sulphide, Na_2S, and potassium sulphide, K_2S, do not act upon stannous sulphide, but alkali persulphides convert it into the corresponding sulphostannates.

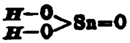
Stannous sulphide, SnS (tin monosulphide), when precipitated, is an amorphous dark brown powder. When formed by direct combination of tin and sulphur, as when tin foil ignites spontaneously in sulphur vapor, it forms a gray crystalline mass. It combines with sulphur to form stannic sulphide, and it is acted upon by solutions of sulphides containing free sulphur, and by solutions of persulphides, with formation of *sulphostannates*.

α-Stannic Hydroxides, and α-Stannic Acids.

By the action of suitable reagents upon stannic salts, the α-stannic hydroxides or α-stannic acids may be formed.



When to a solution of stannic chloride, $SnCl_4$, sodium hydroxide is added in suitable proportion, a white precipitate is formed which may contain the normal *α-stannic hydroxide*, $Sn(OH)_4$, but which yields upon analysis *α-stan-*



$\mathrm{(H{-}O)_2{>}Sn{=}O}$

nic oxyhydroxide, $SnO(OH)_2$, known more commonly as *α-stannic acid*, H_2SnO_3.

$$SnCl_4 + 4\,NaOH = \mathbf{Sn(OH)_4} + 4\,NaCl$$
$$SnCl_4 + 4\,NaOH = \mathbf{SnO(OH)_2} + H_2O + 4\,NaCl$$

The α-stannic acid may also be obtained as a precipitate by acting upon stannic chloride with a suitable proportion of sodium carbonate, carbon dioxide being evolved.

$$SnCl_4 + 2\,Na_2CO_3 + H_2O = \mathbf{SnO(OH)_2} + 4\,NaCl + 2\,CO_2$$

The precipitate of α-stannic acid is readily acted upon by sodium hydroxide with the formation of *sodium stannate*, $Na_2SnO_3 \cdot 3\,H_2O$, in solution, and a sufficient excess of these reagents will therefore prevent the precipitation of the α-stannic acid.

Many salts of strongly electro-positive elements are capable of precipitating stannic acid by action upon stannic chloride. Calcium carbonate, barium carbonate, and sodium sulphate are such salts. Thus, by the action upon stannic chloride, $SnCl_4$, of a concentrated solution of sodium sulphate, a precipitate is obtained which when dried in air has the composition of α-stannic oxyhydroxide, $SnO(OH)_2$.

$$SnCl_4 + 4\,Na_2SO_4 + 3\,H_2O = \mathbf{SnO(OH)_2} + 4\,NaCl + 4\,NaHSO_4$$

Stannic Salts.

By the action of certain acids upon the α-stannic hydroxides stannic salts are formed in which tin is the positive ion. Thus sulphuric acid acts upon α-stannic oxyhydroxide, $SnO(OH)_2$, to form *stannic sulphate*, $Sn(SO_4)_2$,

$$SnO(OH)_2 + 2\,H_2SO_4 = Sn(SO_4)_2 + 3\,H_2O$$

sufficiently dilute nitric acid forms *stannic nitrate*, $Sn(NO_3)_4$,

$$SnO(OH)_2 + 4\,HNO_3 = Sn(NO_3)_4 + 3\,H_2O$$

and hydrochloric acid forms *stannic chloride*, $SnCl_4$.

$$SnO(OH)_2 + 4\,HCl = SnCl_4 + 3\,H_2O$$

The stannic sulphate and stannic nitrate thus formed are easily hydrolyzed in solution, with formation of an insoluble gelatinous precipitate of α-stannic acid. In reacting with acids to form stannic salts stannic hydroxide plays the part of a weak base.

ates. By neutralizing the α-stannic acid with basic hydroxi uble α-stannates are formed in which tin is in the **negative ion.**

>Sn=0 Thus, by acting upon α-stannic acid, H_2SnO_3, with sodium hydroxide, we obtain *sodium* **α-stannate,** nO_3, in solution.

$$2\,NaOH + H_2SnO_3 = Na_2SnO_3 + 2\,H_2O$$

similar manner we may produce a potassium α-metastannate, K_2SnO_3, solution.

The *sodium stannate* of commerce, employed as "**preparing salt**" in calico-printing, is made by heating tin with sodium hydroxide and sodium nitrate, or by fusing stannic oxide with sodium hydroxide. Sodium stannate forms crystals of the composition $Na_2SnO_3 \cdot 3\,H_2O$, and also of the composition $Na_2SnO_3 \cdot 10\,H_2O$. By similar processes *potassium stannate* may be formed as crystals of the composition $K_2SnO_3 \cdot 3\,H_2O$.

In its action with basic hydroxides to form stannates in which tin is negative the stannic hydroxides act like weak acids, and by regulated action of the common acids upon solutions of α-stannates the α-stannic acid is precipitated.

β-Stannic Acid and β-Stannic Salts. *By the action upon tin of concentrated nitric acid, β-stannic hydroxides or β-stannic acids, isomeric with α-stannic acids, may be formed.*

When tin and nitric acid of specific gravity 1.35 enter into reaction there is formed besides soluble stannic nitrate an insoluble white oxyhydroxide, called *β-stannic oxyhydroxide*, $SnO(OH)_2$, or *β-stannic acid*, H_2SnO_3, and having the composition represented by the symbols of α-stannic oxyhydroxide, or α-stannic acid, but differing in many particulars from that acid.

$$Sn + 4\,HNO_3 = SnO(OH)_2 + 4\,NO_2 + H_2O$$

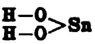
This stannic hydroxide is unaffected when treated with an excess of sodium hydroxide, and is acted upon by boiling hydrochloric acid to form a *β-stannic chloride*, unacted upon by the excess of hydrochloric acid but soluble in water.

When a solution of β-stannic chloride is treated with sodium hydroxide, a *sodium β-stannate* is precipitated which is unacted upon by an excess of sodium hydroxide. Sodium β-stannates corresponding to the symbols $H_8Na_2Sn_5O_{15}$ and $H_{16}Na_2Sn_9O_{27}$, and other similar β-stannates, are known. It is probable that β-stannic acid is a polymeric form of α-stannic ac

Both α-stannic acid and α-stannic chloride tend to go over spontaneously into the form of β-stannic acid and β-stannic chloride, respectively. Thus, a precipitate of α-stannic acid gives after a time reactions characteristic of β-stannic acid, and a solution of α-stannic chloride tends to show likewise the properties of β-stannic chloride, one of which is to give a yellow color with colorless stannous chloride though itself colorless. Both α-stannic acid and β-stannic acid lose water when heated and yield *stannic oxide*, SnO_2, as a final product of dehydration.

The appearance of two stannic acids of identical composition was the first recognized instance of *isomerism* among chemical compounds. It was observed in 1811 by Berzelius, and investigated by Davy and Gay-Lussac in 1817. The exact constitution of these isomers has, however, never been proved.

Stannous Hydroxide. *Stannous hydroxide may be formed by acting upon stannous salts with soluble basic hydroxides or carbonates.*


$$\begin{matrix} H-O \\ H-O \end{matrix}>Sn$$

Sodium hydroxide, in suitable proportions, precipitates from a solution of stannous chloride, $SnCl_2$, white *stannous hydroxide*, $Sn(OH)_2$, which decomposes to form a *stannous oxyhydroxide*, $Sn_2O(OH)_2$,

$$SnCl_2 + 2\,NaOH = \mathbf{Sn(OH)_2} + 2\,NaCl$$

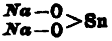
and a similar precipitate may be obtained by acting upon stannous chloride with sodium carbonate in proper proportions.

$$SnCl_2 + Na_2CO_3 + H_2O = \mathbf{Sn(OH)_2} + 2\,NaCl + CO_2$$

By heating the precipitate of stannous hydroxide water is evolved, and under conditions which prevent oxidation *stannous oxide*, SnO, is obtained as a final product.

The precipitate of stannous hydroxide is acted upon by the common acids and by basic hydroxides. Sulphuric acid, when sufficiently dilute, forms the unstable *stannous sulphate*, $SnSO_4$,

$$Sn(OH)_2 + H_2SO_4 = SnSO_4 + 2\,H_2O$$


$$\begin{matrix} Na-O \\ Na-O \end{matrix}>Sn$$

and sodium hydroxide forms unstable *sodium stannite*, Na_2SnO_2, in solution,

$$2\,NaOH + H_2SnO_2 = Na_2SnO_2 + 2\,H_2O$$

which decomposes when heated, with formation of sodium stannate, Na_2SnO_3, and tin.

$$2\,Na_2SnO_2 + H_2O = Na_2SnO_3 + 2\,NaOH + Sn$$

ides. *The oxides of tin may be formed by the direct oxidation of tin, and by the decomposition of the tin hydroxides by heating.*

When tin is heated to white heat in air, **stannic oxide**, SnO_2 (tin dioxide), is formed as an amorphous **white pow-**, yellow when hot, insoluble in water, infusible, not **readily attacked** acids.

$$Sn + O_2 = SnO_2$$

Stannic oxide is also produced when either α- or **β-stannic acid**, H_2SnO_3, is heated, $H_2SnO_3 = SnO_2 + H_2O$

or when the precipitate formed by acting upon tin **with concentrated** nitric acid is washed and ignited.

Stannic oxide is found native as *cassiterite* or **"tin stone," which** forms opaque steel-gray prismatic crystals, of **specific gravity 6.8.** It is the principal ore of tin, and is reduced to tin by **hydrogen or carbon.**

Sn=0 *Stannous oxide*, SnO (tin monoxide), **is formed as a** black crystalline powder when **stannous hydroxide, $Sn(OH)_2$,** or the basic compound, $Sn_2O(OH)_2$, is heated out of **contact with** air,

$$Sn(OH)_2 = SnO + H_2O$$

as when the precipitate formed by acting upon stannous **chloride with** sodium carbonate is washed in absence of air, and dried at 80° in an atmosphere of hydrogen or carbon dioxide.

Stannous oxide absorbs oxygen from the air **spontaneously, and takes fire when heated in air**, forming stannic oxide.

$$2\ SnO + O_2 = 2\ SnO_2$$

It is acted upon by acids, forming stannous salts. It yields soluble stannates when fused with basic hydroxides or carbonates, and is reduced to tin by hydrogen or carbon.

Summary. *We observe in regard to tin that the metal is acted upon by sulphuric acid, nitric acid, and hydrochloric acid, under suitable conditions of dilution, with formation of soluble stannic salts and stannous salts which, with the exception of stannous chloride, are readily hydrolyzed. Stannic chloride and stannous chloride may be formed in anhydrous condition by combination of tin with chlorine, and either of these compounds may be converted into the other by suitable means. Both form double chlorides.*

Insoluble stannic sulphide and stannous sulphide may be formed by adding soluble sulphides to solutions of corresponding stannic or stannous salts. Stannic sulphide combines with ammonium sulphide and alkali sulphides to form soluble sulphostannates. Stannous sulphide combines with persulphides to form sulphostannates.

The insoluble stannic hydroxide and stannic oxyhydroxide, known as stannic acids, exist in two isomeric forms. The hydroxide precipitated from stannic salt solutions, consisting of the α-stannic acids, is acted upon by acids with formation of stannic salts, and by bases with formation of stannates; the hydroxide formed by acting upon tin with nitric acid, known as the β-stannic acid, is not readily acted upon by acids, and forms with bases stannates of complex constitution. The α-stannic acid is spontaneously convertible into the β-stannic acid. The α- and β-stannates are decomposed by acids with formation of stannic acids. The insoluble stannous hydroxide, readily decomposed by heat and acted upon by acids, may be formed as a precipitate.

The insoluble stannic oxide and stannous oxide may be made by decomposing the respective hydroxides, and stannic oxide is formed when tin is heated in air. Both oxides may be acted upon by acids and by bases, and may be reduced to tin by suitable reagents.

Lead, Pb, 206.9

Reduction of Lead Ores. When *galenite*, PbS (galena), is heated in air, lead oxide, PbO (litharge), or lead sulphate, $PbSO_4$, may be formed according to the degree of oxidation.

$$2\,PbS + 3\,O_2 = 2\,PbO + 2\,SO_2$$
$$PbS + 2\,O_2 = PbSO_4$$

The lead oxide or lead sulphate thus formed may be reduced to lead by heating with an excess of lead sulphide, PbS.

$$2\,PbO + PbS = 3\,Pb + SO_2$$
$$PbSO_4 + PbS = 2\,Pb + 2\,SO_2$$

Or, lead sulphide may be reduced to lead directly by heating it with iron.

$$PbS + Fe = FeS + Pb$$

These reactions form the basis of the *metallurgical processes* by which lead is obtained from its ores. Pure galena ores are treated by the *air reduction process*, in which the ores are roasted in a reverberatory furnace, while lead ores which contain compounds of other metals may be heated with carbonaceous material. Sometimes blast furnaces or hearths may be employed in smelting lead ores. We have already considered the concentration and cupellation processes by which silver and lead are separated from ores in which compounds of both elements occur.

Properties of Lead.

Lead is a bluish white metal, soft and tough, somewhat ductile, but not very tenacious. It ordinarily has a specific gravity of 11.37, and melts at from 325° to 335°, flowing readily, and vaporizes at white heat, about 1700°. It is a poor conductor of electricity. By allowing a mass of molten lead to partly solidify, and then pouring away the portion still liquid, octahedral crystals may be formed.

Lead is slowly acted upon by air, becoming covered with a film of dark colored oxide; and by heating lead more or less strongly in air several oxides may be formed. Lead is not acted upon by pure water, but water containing air will slowly act upon it, forming a slightly soluble hydroxide; and with water containing carbon dioxide the action is marked at first, but is finally impeded by the incrustation of the surface of the lead with a carbonate, which, however, in the presence of much carbon dioxide, is somewhat soluble. The action of impure water upon lead is aided by the presence of nitrates and chlorides, but seems to be retarded by sulphates. Lead is acted upon very slowly by hot concentrated hydrochloric acid with evolution of hydrogen, by hot concentrated sulphuric acid with evolution of sulphur dioxide, and by nitric acid with evolution of nitrogen oxides, the corresponding salts, in which lead is the positive ion, being formed in each case. Lead combines directly with the halogen elements and with sulphur to form binary compounds, and with antimony, bismuth, copper, zinc, tin, and other metals to form useful alloys.

Lead compounds act as a cumulative poison when taken into the system continuously in small amounts. The use of lead pipes for conducting water used for drinking and for culinary purposes may, under certain conditions, be a source of danger. Although the presence of certain salts in water may decrease the solubility of the lead, and although the deposit from hard water may incrust the interior of the lead pipe with a protective coating, the presence of certain gases, such as oxygen, carbon dioxide, and ammonia, may increase the action of the water upon the lead. Rain water especially is liable to exert a solvent action upon lead pipes.

Uses of Lead. On account of its resistance to the action of air and water and the common acids, lead is employed in making vessels of various sorts, and in *lead pipes* which are used for carrying water. The most important lead alloys are the *soft solders* and *pewters*, containing tin and lead; *type-metal*, containing usually lead and antimony, and sometimes tin, and other metals in smaller proportions; and *shot-metal*, consisting of lead and a small proportion of arsenic.

In the process of making *shot*, the lead is melted in a cast iron pan, and after the addition of a sufficient amount of lead arsenide to form an alloy containing from 0.8 to 0.9 per cent. of arsenic, the molten alloy is poured into a perforated iron basin at the top of a high *tower*, and allowed to fall into a dilute solution of sodium sulphide. The presence of arsenic makes the drops of molten alloy very fluid, so that they assume a spherical form in their passage to the bottom of the tower. The effect of the sodium sulphide is to coat the shot with a thin layer of lead sulphide which prevents superficial oxidation when the shot are removed from the water. Shot are sometimes made by allowing the molten metal to fall through an ascending air current, or by pouring it in a thin stream upon a rapidly revolving disk, when the centrifugal action divides the metal into drops, which are thrown against a surrounding screen.

Lead Oxides. *Lead forms five oxides: lead suboxide, lead monoxide, red lead oxide, lead sesquioxide, and lead dioxide, all of which may be formed by the suitable oxidation of lead or lead compounds.*

$\begin{matrix}Pb\\Pb\end{matrix}>O$ *Lead suboxide*, Pb_2O, is formed as a dark film upon a clean surface of lead which is exposed to the action of the air,

$$4\,Pb + O_2 = 2\,Pb_2O$$

and the same compound may be formed as a black powder by decomposing lead oxalate, PbC_2O_4, by heating below 300° out of contact of air. When heated in air, lead suboxide forms lead monoxide.

$$2\,Pb_2O + O_2 = 4\,PbO$$

$Pb=O$ *Lead monoxide*, PbO (litharge), formed when lead is heated in air to its point of volatilization, is a heavy yellow or reddish yellow powder, of specific gravity 9.36, becoming

$$2\ Pb + O_2 = 2\ PbO$$

When heated with hydrogen or carbon, lead monoxide is reduced to lead.

$$PbO + H_2 = Pb + H_2O$$

When fused and allowed to cool, it forms octahedral crystals, and similar crystals of lead oxide occur native as the mineral *massicot.*

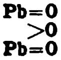
Lead monoxide is obtained as a commercial product by direct oxidation of lead in the metallurgical processes by which lead is separated from silver, and by heating certain lead salts such as lead nitrate and lead carbonate. It is employed to give refractivity to flint glass, such as is used in optical instruments. It is also employed in preparing many salts of lead.

Pb_3O_4

Red lead oxide, Pb_3O_4 (lead orthoplumbate, red lead), may be obtained as a scarlet, crystalline, granular powder, of specific gravity 8.6 to 9.1, by heating lead monoxide, PbO, to dull red heat in an excess of air, for several hours.

$$6\ PbO + O_2 \rightleftarrows 2\ Pb_3O_4$$

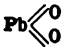
When red lead is heated to bright redness in the air, it evolves oxygen, forming lead monoxide, PbO. Red lead is found native as the mineral *minium.*



$$\begin{matrix}Pb{=}O\\ \ \ >O\\ Pb{=}O\end{matrix}$$

Lead sesquioxide, Pb_2O_3, is precipitated as a reddish yellow amorphous powder when sodium hypochlorite is added in suitable proportions to the solution prepared by adding to lead nitrate solution sufficient potassium hydroxide to act upon the lead hydroxide at first precipitated.

$$2\ Pb(OH)_2 + NaOCl = Pb_2O_3 + NaCl + 2\ H_2O$$



Lead dioxide, PbO_2 (lead peroxide), is generally an amorphous, dark brown powder of specific gravity 8.9 to 9.2. It may, however, be prepared in crystalline condition and occurs naturally as the mineral *plattnerite* in hexagonal prisms. It may be formed by heating to 110° the deposit upon the anode of an electrolytic cell in which oxygen ions are produced in presence of a salt of lead, notably in a solution of lead nitrate strongly acidulated with nitric acid.

$$2\ Pb(NO_3)_2 + O_2 + 2\ H_2O = 2\ PbO_2 + 4\ HNO_3$$

It is formed when a mixture of freshly precipitated lead carbonate and an alkali carbonate is acted upon by an excess of chlorine.

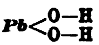
$$PbCO_3 + Na_2CO_3 + Cl_2 = PbO_2 + 2\,NaCl + 2\,CO_2$$

It may be prepared by fusing lead monoxide with potassium chlorate, $KClO_3$, or potassium nitrate, KNO_3. It is, however, most readily obtained as a residue left by acting upon red lead oxide, Pb_3O_4, with nitric acid, which acts upon a part of the lead oxide to form lead nitrate, $Pb(NO_3)_2$. When heated strongly, lead dioxide evolves oxygen, leaving lead monoxide.

$$2\,PbO_2 = 2\,PbO + O_2$$

In sunlight it undergoes partial decomposition, with formation of red lead oxide. The ease with which it gives up oxygen makes it useful as an oxidizer.

Lead Hydroxides. *Hydroxides of lead are known, corresponding to lead monoxide and lead dioxide.*


$Pb<^{O-H}_{O-H}$

When sodium hydroxide or other alkali hydroxide is added to a solution of lead nitrate, $Pb(NO_3)_2$, or a similar lead salt, a white precipitate of *lead hydroxide*, $Pb(OH)_2$, or *lead oxyhydroxide*, $Pb_2O(OH)_2$, is obtained, according to the conditions, which may be acted upon by an excess of an alkali hydroxide, and by acids, and may be decomposed by heating.

$$Pb(NO_3)_2 + 2\,NaOH = Pb(OH)_2 + 2\,NaNO_3$$

Ammonium hydroxide added to a solution of lead nitrate precipitates white $Pb_2O(NO_3)_2$, while with a solution of lead acetate it forms a basic lead acetate.

By the electrolysis of a suitable salt of lead under regulated conditions of current and temperature *metaplumbic acid*, H_2PbO_3, may be obtained, and this yields lead dioxide when heated to 110°.

Action of Acids upon Lead Oxides. *All the oxides and hydroxides of lead are acted upon by certain acids, to form the common salts of lead, in which lead is a positive bivalent ion.*

From lead monoxide many salts may be prepared by the action of the appropriate acids. Thus lead monoxide is acted upon by hydrochloric acid, with formation of *lead chloride*, $PbCl_2$,

$$PbO + 2\,HCl = PbCl_2 + H_2O$$

by sulphuric acid with formation of *lead sulphate*, $PbSO_4$,

$$PbO + H_2SO_4 = PbSO_4 + H_2O$$

by nitric acid with formation of *lead nitrate*, $Pb(NO_3)_2$,

$$PbO + 2\,HNO_3 = Pb(NO_3)_2 + H_2O$$

and by acetic acid with formation of *lead acetate*, $Pb(C_2H_3O_2)_2$.

$$PbO + 2\,H(C_2H_3O_2) = Pb(C_2H_3O_2)_2 + H_2O$$

When oxides of lead other than lead monoxide are acted upon by acids, the tendency to form salts corresponding to the monoxide is striking. Thus, hydrochloric acid acts upon lead suboxide to form *lead chloride*, $PbCl_2$, and lead.

$$Pb_2O + 2\,HCl = PbCl_2 + Pb + H_2O$$

Lead dioxide, PbO_2, is acted upon by hydrochloric acid at ordinary temperatures with formation of *lead chloride*, $PbCl_2$, and liberation of chlorine,

$$PbO_2 + 4\,HCl = PbCl_2 + Cl_2 + 2\,H_2O$$

though when the action takes place in cold solution of the concentrated acid there is formed an unstable *lead tetrachloride*, $PbCl_4$.

$$PbO_2 + 4\,HCl = PbCl_4 + 2\,H_2O$$

Upon adding ammonium chloride to a mixture of lead dioxide and hydrochloric acid, the double salt, $PbCl_4 \cdot 2\,NH_4Cl$, separates as yellow crystals, which react with ice-cold concentrated sulphuric acid to form ammonium sulphate, hydrochloric acid, and lead tetrachloride, which collects beneath the sulphuric acid as a yellow oil, becoming crystalline at − 15°, and decomposing gradually at ordinary temperatures into lead chloride and chlorine. Sulphuric acid acts upon lead dioxide to form *lead sulphate*, $PbSO_4$, with liberation of oxygen.

$$2\,PbO_2 + 2\,H_2SO_4 = 2\,PbSO_4 + O_2 + 2\,H_2O$$

Nitric acid does not act upon lead dioxide.

Lead sesquioxide, Pb_2O_3, when acted upon by nitric acid, yields *lead nitrate*, $Pb(NO_3)_2$, and lead dioxide, PbO_2.

$$Pb_2O_3 + 2\,HNO_3 = Pb(NO_3)_2 + PbO_2 + H_2O$$

Red lead oxide, Pb_3O_4, is acted upon by hydrochloric acid with formation of *lead chloride*, $PbCl_2$, and liberation of chlorine,

$$Pb_3O_4 + 8\,HCl = 3\,PbCl_2 + Cl_2 + 4\,H_2O$$

by hot concentrated sulphuric acid with formation of *lead sulphate*, $PbSO_4$, and liberation of oxygen,

$$2\,Pb_3O_4 + 6\,H_2SO_4 = 6\,PbSO_4 + O_2 + 6\,H_2O$$

by dilute sulphuric acid with formation of *lead sulphate*, $PbSO_4$, and lead dioxide, PbO_2,

$$Pb_3O_4 + 2\,H_2SO_4 = 2\,PbSO_4 + PbO_2 + 2\,H_2O$$

and by nitric acid with formation of *lead nitrate*, $Pb(NO_3)_2$, and lead dioxide, PbO_2.

$$Pb_3O_4 + 4\,HNO_3 = 2\,Pb(NO_3)_2 + PbO_2 + 2\,H_2O$$

Action of Acids upon Lead

Certain salts of lead in which lead is the positive ion may likewise be formed by the action of appropriate acids upon lead. Thus, by the action of nitric acid upon lead white soluble *lead nitrate*, $Pb(NO_3)_2$, is formed, and nitrogen oxides are evolved.

$$Pb + 4\,HNO_3 = Pb(NO_3)_2 + 2\,H_2O + 2\,NO_2$$

If the nitric acid employed is sufficiently concentrated, the lead nitrate formed may remain undissolved so as to impede the action, which will, however, continue when the lead nitrate is dissolved by adding water.

Though cold concentrated sulphuric acid acts upon lead very slowly, and the dilute acid not at all, hot concentrated sulphuric acid attacks lead with evolution of sulphur dioxide and formation of white *lead sulphate*, $PbSO_4$, which is precipitated upon addition of water.

$$Pb + 2\,H_2SO_4 = PbSO_4 + SO_2 + 2\,H_2O$$

Hydrochloric acid slowly attacks lead with evolution of hydrogen and formation of white moderately soluble *lead chloride*, $PbCl_2$, which may remain in solution in the presence of an excess of acid.

$$Pb + 2\,HCl = PbCl_2 + H_2$$

Insoluble Lead Salts.

Certain insoluble salts of lead in which lead is the positive ion may be formed as precipitates by the action of suitable reagents upon solutions of lead salts.

en to a solution of lead nitrate, $Pb(NO_3)_2$, hydrochl
, or a soluble chloride, is added, a white precipitate of *lead chlorid*
l_2, slightly soluble in cold water, freely soluble in hot water, is ob
ed.

$$Pb(NO_3)_2 + 2\,HCl = \mathbf{PbCl_2} + 2\,HNO_3$$

Sulphuric acid and soluble sulphates precipitate from lead nitrat
olution white *lead sulphate*, $PbSO_4$, which is slightly acted upon by co
centrated acids, more readily by alkali hydroxides.

$$Pb(NO_3)_2 + H_2SO_4 = \mathbf{PbSO_4} + 2\,HNO_3$$

Hydrogen sulphide, and other soluble sulphides, precipitate fro
lead nitrate solution brownish black *lead sulphide*, PbS, not attacked
alkali hydroxides or by dilute acids, but acted upon by strong nitric ac

$$Pb(NO_3)_2 + H_2S = \mathbf{PbS} + 2\,HNO_3$$

Sodium carbonate and other soluble carbonates precipitate fr
lead nitrate solution a white *lead hydroxycarbonate*, the composi
of which is dependent upon the conditions, but which in concentra
hot solution consists chiefly of $Pb_3(OH)_2(CO_3)_2$.

$$3\,Pb(NO_3)_2 + H_2O + 3\,Na_2CO_3 = \mathbf{Pb_3(OH)_2(CO_3)_2} + CO_2 + 6\,Na$$

Potassium chromate, K_2CrO_4, or potassium dichrom
$K_2Cr_2O_7$, precipitates from a solution of lead nitrate, yellow
chromate, $PbCrO_4$, acted upon by alkali hydroxides and by concentr
acids.

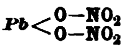
$$Pb(NO_3)_2 + K_2CrO_4 = \mathbf{PbCrO_4} + 2\,KNO_3$$

Lead iodide, PbI_2, *lead sulphite*, $PbSO_3$, *lead thiosulphate*, PbS_2O
lead ferrocyanide, $Pb_2Fe(CN)_6$, may also be precipitated by ad
suitable reagents to solutions of lead salts.

Lead Salts. *The common salts of lead, in which lead is the positi*
may be formed by the action of acids upon lead or upo
oxides, or by precipitation from solutions of lead compounds.

$Pb<^{Cl}_{Cl}$ *Lead chloride*, $PbCl_2$, formed by the action of hydro
acid upon lead or lead oxides, or by the action of c
upon lead, or by the interaction of hydrochloric acid or a soluble
with a soluble lead salt, is a white salt, soluble in hot water, s
30 times its weight of cold water, crystallizing in white needles
at 500°, volatilizing at white heat, forming a vapor of a speci

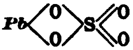
corresponding to the symbol given. It is acted upon by ammonium hydroxide with formation of an insoluble basic salt.



$Pb<\begin{matrix}O-NO_2\\O-NO_2\end{matrix}$

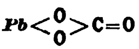
Lead nitrate, $Pb(NO_3)_2$, formed by the action of nitric acid upon lead or upon lead oxides, is a white salt, crystallizing in octahedra, moderately soluble in water, forming when boiled with water an insoluble *lead hydroxynitrate*, $Pb(OH)NO_3$, and decomposed by heating into lead monoxide, nitrogen tetroxide, and oxygen.

$$2\,Pb(NO_3)_2 = 2\,PbO + 4\,NO_2 + O_2$$



Lead sulphate, $PbSO_4$, formed by the action of sulphuric acid upon lead or lead oxide, or by the action of sulphuric acid or soluble sulphates upon solution of lead salts, is a white crystalline salt, slightly soluble in water, and very insoluble in dilute sulphuric acid. It may be reduced to lead sulphide, PbS, by heating with carbon. It occurs as the mineral *anglesite*.

$$PbSO_4 + 2\,C = PbS + 2\,CO_2$$

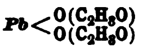


$Pb<\begin{matrix}O\\O\end{matrix}>C=O$

Lead carbonate, $PbCO_3$, occurs as the mineral *cerussite*. The basic lead carbonate formed as a precipitate by adding soluble carbonates to solutions of lead salts, and which approximates to the composition $Pb_3(OH)_2(CO_3)_2$, is the "white lead" largely used as a pigment. It is manufactured by acting upon lead monoxide with acetic acid, and by passing carbon dioxide into the lead acetate thus formed. Lead carbonate is acted upon superficially by hydrogen sulphide with formation of black lead sulphide. Pictures painted in white oil colors containing lead carbonate often become darkened upon exposure to the air contaminated by the products of the burning of illuminating gas and other fuels containing sulphur.

$Pb=S$

Lead sulphide, PbS, formed by the action of hydrogen sulphide or of soluble sulphides upon solutions of lead salts, is an amorphous black powder. In the presence of an excess of hydrochloric acid a red compound, $PbS \cdot PbCl_2$, may be precipitated by hydrogen sulphide from solution of lead salts. Lead sulphide may be acted upon by moderately dilute nitric acid with formation of lead nitrate and the liberation of nitrogen oxides, sometimes with precipitation of sulphur. Lead sulphide occurs as the mineral *galenite* (galena) in the form of glistening cubes or octahedra.



$Pb<\begin{matrix}O(C_2H_3O)\\O(C_2H_3O)\end{matrix}$

Lead acetate, $Pb(C_2H_3O_2)_2$ (sugar of lead), is formed by the action of acetic acid, $H(C_2H_3O_2)$, upon lead oxide.

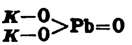
$$PbO + 2\,H(C_2H_3O_2) = Pb(C_2H_3O_2)_2 + H_2O$$

It may be obtained as brilliant prismatic crystals of the composition $Pb(C_2H_3O_2)_2 \cdot 3\,H_2O$, which lose water on exposure. By heating a water solution of lead acetate with lead monoxide, basic acetates, such as $Pb(OH)(C_2H_3O_2)$ and $Pb_3O_2(C_2H_3O_2)$, may be obtained. By the action of hot acetic acid upon red lead, Pb_3O_4, *lead tetraacetate*, $Pb(C_2H_3O_2)_4$, may be formed. Lead acetate absorbs carbon dioxide from the air, forming lead carbonate.

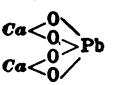
Plumbites and Plumbates.

Lead monoxide and lead dioxide react with alkali hydroxides with the formation of salts in which lead is a constituent of the negative ion.

Lead monoxide, PbO, is acted upon by a hot solution of an alkali hydroxide to form a colorless solution; and lead hydroxide, $Pb(OH)_2$, formed by precipitation from a lead salt by an alkali hydroxide, is readily acted upon by an excess of the alkali hydroxide. Such action points to the existence of more or less unstable alkali *plumbites.* Lead dioxide is acted upon by a warm solution of potassium hydroxide, and from the solution on cooling crystals of *potassium metaplumbate*, $K_2PbO_3 \cdot 3\,H_2O$, separate. Other *plumbates* may be formed similarly.



$\begin{matrix}K-O\\K-O\end{matrix}>Pb=O$



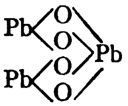
$\begin{matrix}Ca<\begin{matrix}O\\O\end{matrix}\\Ca<\begin{matrix}O\\O\end{matrix}\end{matrix}>Pb$

By heating lead dioxide, PbO_2, with calcium oxide, CaO, or calcium carbonate, $CaCO_3$, or by heating lead monoxide with calcium oxide in the presence of air, *calcium orthoplumbate*, Ca_2PbO_4, may be obtained as a yellowish red salt.

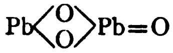
$$PbO_2 + 2\,CaO = Ca_2PbO_4$$

The withdrawal of oxygen from the air by the action of lead oxide in forming a plumbate, from which the oxygen may be again evolved by heating in presence of carbon dioxide, has been applied to the commercial production of oxygen by *Kassner's method.*

When a solution of potassium metaplumbate, K_2PbO_3, is mixed with a solution of lead monoxide in potassium hydroxide, red lead oxide, Pb_3O_4, is precipitated, and this oxide may be regarded as a lead salt of the hypothetical *orthoplumbic acid*, H_4PbO_4, corresponding to the symbol



Lead sesquioxide, Pb_2O_3, may, in like manner, be regarded as the lead salt of a hypothetical *metaplumbic acid*, H_2PbO_3, corresponding to the symbol



$$Pb\genfrac{}{}{0pt}{}{\diagup O \diagdown}{\diagdown O \diagup}Pb{=}O$$

Summary. *Lead forms five oxides: lead suboxide, formed by exposure of clean lead to air; lead monoxide, made by heating lead in air; red lead oxide, formed by heating lead monoxide in air; lead sesquioxide, formed by oxidizing a lead salt by sodium hypochlorite; and lead dioxide, formed by oxidizing a lead salt by electrolysis or by the action of chlorine. Lead hydroxide, corresponding to lead oxide, may be formed as a precipitate from solutions of lead salts; and metaplumbic acid, corresponding to lead dioxide, may be obtained by electrolyzing a lead salt under suitable conditions.*

Lead chloride, lead sulphate, lead nitrate, and lead acetate may be formed by the action of the appropriate acids upon lead monoxide. By the action of hydrochloric acid upon lead dioxide, lead chloride is ordinarily formed, while chlorine is evolved, although in the cold lead tetrachloride may be formed. By the action of sulphuric acid upon lead dioxide, lead sulphate is formed and oxygen liberated. Both lead sesquioxide and red lead oxide are acted upon by nitric acid with formation of lead nitrate and lead dioxide. Hydrochloric acid acts upon red lead oxide to form lead chloride and liberate chlorine, while sulphuric acid acts upon the same oxide to form lead sulphate and liberate oxygen, or with the formation of lead sulphate and lead dioxide.

Lead is acted upon by nitric acid with the formation of lead nitrate, by hot concentrated sulphuric acid with formation of lead sulphate, and slowly by hydrochloric acid with formation of lead chloride.

Lead chloride, lead sulphate, lead sulphide, basic lead carbonate, lead chromate, lead iodide, and other lead salts may be formed as precipitates.

Lead monoxide is acted upon by potassium hydroxide with formation of a solution which suggests the existence of unstable plumbites. Lead dioxide is acted upon by potassium hydroxide with formation of potassium plumbate, and other plumbates may be similarly made.

CHAPTER XV

SECONDARY SERIES—GROUP V

VANADIUM, V, 51.2

COLUMBIUM (NIOBIUM), Cb, 94

TANTALUM, Ta, 183

THE elements of Group V are lustrous gray solids found in combination in a few minerals and obtained by reduction of halogen compounds. Vanadium occurs native in vanadates of the metals, of which one is the mineral *vanadinite* $Pb_4(PbCl)(VO_4)_3$, a lead vanadate containing chlorine. Columbium and tantalum generally occur together in combination in certain rare minerals, columbates and tantalates, such as *columbite* (Fe, Mn)(Cb, Ta)$_2$O$_6$, and *tantalite*, chiefly (Fe, Mn)Ta_2O_6.

By treating *vanadinite* with nitric acid, precipitating lead sulphide by hydrogen sulphide, evaporating the solution after filtration, and igniting the residue, reddish brown *vanadium pentoxide*, V_2O_5, may be obtained, from which *orthovanadates*, such as Na_3VO_4, *pyrovanadates*, such as $Na_4V_2O_7$, and *metavanadates*, such as $NaVO_3$, may be made. From vanadium pentoxide may be obtained blue *vanadium tetroxide*, V_2O_4, black *vanadium trioxide*, V_2O_3, gray *vanadium dioxide*, V_2O_2, and brown *vanadium monoxide*, V_2O. Vanadium forms a yellow oxychloride, $VOCl_3$, known as *vanadyl chloride*, liquid at ordinary temperatures; a green crystalline oxychloride, $VOCl_2$, and a brown oxychloride, VOCl; and also *vanadium tetrachloride*, VCl_4, a brown liquid; *vanadium trichloride*, VCl_3, crystalline and violet-red; *vanadium dichloride*, VCl_2, greenish and crystalline. From vanadium dichloride may be obtained elementary *vanadium*, gray, rapidly oxidizable in the air when heated and slowly attacked when cold, and capable of combining with nitrogen at red heat to form the yellowish brown *vanadium nitride*, VN, of metallic luster. *Vanadium sulphides*, V_2S_2 and V_2S_3, are known, and so are certain compounds obtained by acting with sulphuric acid upon vanadium pentoxide, as $V_2O_2(SO_4)_2$, in which vanadium tetroxide apparently shows weak basic tendencies and forms a union with the SO_4-ion.

Columbium forms yellowish white *columbium pentoxide*, Cb_2O_5; blue-black *columbium tetroxide*, Cb_2O_4; and white *columbium dioxide*, Cb_2O_2; *columbium pentachloride*, $CbCl_5$, crystallizing in yellow needles and easvolatilized ; *columbium trichloride*, $CbCl_3$, dark and crystalline ; and *columbium oxychloride*, $CbOCl_3$, colorless and crystalline. From columbium pentoxide complex *columbates*, derivatives of the acid H_3CbO_4, may be obtained, and certain crystalline double fluorides and oxyfluorides, such as $2\ KF \cdot CbF_5$ and $2\ KF \cdot CbOF_3$, are characteristic. From the columbium chlorides by reduction by hydrogen may be obtained the element *columbium*, a gray, brilliant solid.

Tantalum forms white *tantalum pentoxide*, Ta_2O_5 ; dark gray *tantalum tetroxide*, Ta_2O_4 ; *tantalum pentachloride*, $TaCl_5$, light yellow and crystalline ; crystalline double fluorides and oxyfluorides, such as $2\ KF \cdot TaF_5$ and $2\ KF \cdot TaOF_3$; and *tantalates* derived from the acid H_3TaO_4.

CHAPTER XVI

SECONDARY SERIES—GROUP VI

Chromium, Cr, 52.1
MOLYBDENUM, Mo, 96.0
TUNGSTEN, W, 184
URANIUM, U, 238.5

Group VI. THE elements of Group VI of the secondary series are found in combination only, chromium associated with iron in ores, and the other elements in a few rare minerals. The principal chromium minerals are *chromite*, $FeCr_2O_4$, and *crocoite*, $PbCrO_4$. All four elements may be prepared from compounds as hard, lustrous metals, white or nearly white in color, of high specific gravity, unacted upon by air or water at ordinary temperatures, acted upon by acids. The elements all form oxides and corresponding hydroxides which are generally acidic in character, being acted upon by bases with formation of salts in which these elements are in the negative ion, although these same high oxides form some salts in which these elements are positive. Thus in the case of chromium we have *chromates* and *chromites* in which chromium is in the negative ion, and chromium sulphate and other chromium salts in which chromium is positive. The maximum valence of the elements of this group is VI, although they sometimes show a valence of IV, III, or II.

The rare element uranium is of interest because of the recently discovered radio-activity of its salts.

Chromium, Cr, 52.1

Reduction of Chromium Ore. Chromium occurs only in combination with other elements, the chief chromium ore being *chromite*, essentially $FeCr_2O_4$, though the element is found in other minerals notably in *crocoite*, $PbCrO_4$. When chromite is roasted in a reverberatory furnace in mixture with sodium carbonate and lime, and exposed to the action of air, sodium chromate, calcium carbonate, and ferric oxide are formed.

$$4\,FeCr_2O_4 + 8\,Na_2CO_3 + 8\,CaO + 7\,O_2 = 8\,Na_2CrO_4 + 8\,CaCO_3 + 2\,Fe_2O_3$$

Upon extracting the fused mass with water, *sodium chromate*, Na_2CrO_4, is dissolved, from which, upon addition of a suitable amount of sulphuric acid to the concentrated solution, are obtained anhydrous sodium sulphate, which crystallizes first, and somewhat impure *sodium dichromate*, $Na_2Cr_2O_7 \cdot 2\,H_2O$, which deposits from the remaining solution on cooling.

$$2\,Na_2CrO_4 + H_2SO_4 = Na_2SO_4 + Na_2Cr_2O_7 + H_2O$$

From the crude sodium dichromate thus obtained the compounds of chromium may be formed.

By treating the suitably concentrated solution of sodium dichromate with potassium chloride, potassium dichromate is precipitated in crystalline form. By recrystallization *potassium dichromate*, $K_2Cr_2O_7$, may be obtained in pure condition.

$$Na_2Cr_2O_7 + 2\,KCl = K_2Cr_2O_7 + 2\,NaCl$$

When concentrated sulphuric acid is added to a cold concentrated solution of potassium dichromate crystalline *chromium trioxide*, CrO_3, separates, which, though soluble in water, may be washed with strong nitric acid by decantation or on asbestos.

$$K_2Cr_2O_7 + H_2SO_4 = K_2SO_4 + 2\,CrO_3 + H_2O$$

Heated to 250°, chromium trioxide decomposes into green *chromic oxide*, Cr_2O_3, and oxygen.

$$4\,CrO_3 = 2\,Cr_2O_3 + 3\,O_2$$

From chromic oxide, by heating with carbon in the electric furnace or by ignition in mixture with powdered aluminium, *chromium* may be produced in quantity.

$$Cr_2O_3 + 3\,C = 2\,Cr + 3\,CO$$
$$Cr_2O_3 + 2\,Al = 2\,Cr + Al_2O_3$$

Chromium. *Chromium*, a gray, lustrous metal, of specific gravity 6.92, somewhat crystalline in structure, is hard, unaffected by air at ordinary temperatures, fusible in the electric arc but not in the oxyhydrogen flame. Above 0° it is attacked by hydrochloric acid with evolution of hydrogen and the formation of chromous chloride.

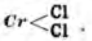
Oxides and Hydroxides. Chromium forms compounds which may be regarded as derivatives of three oxides, and several hydroxides.

[Chromous oxide, CrO]*	Chromous hydroxide, $Cr(OH)_2$
Chromic oxide, Cr_2O_3	Chromic hydroxide, $Cr(OH)_3$
	Chromous acid, $HCrO_2$
Chromium trioxide, CrO_3	Chromic acid, H_2CrO_4†
———	Perchromic acid, $H_2Cr_2O_8$†

* Represented by compounds. † Known in solution.

Corresponding to the hypothetical chromous oxide, CrO, which is not known by itself, and chromous hydroxide, $Cr(OH)_2$, which may be formed by precipitation, we have the *chromous salts*, in which chromium is a bivalent positive ion. Corresponding to chromic oxide, Cr_2O_3, and chromic hydroxide, $Cr(OH)_3$, we have the *chromic salts* in which chromium is a trivalent positive ion; and corresponding to the chromous oxyhydroxide, $HCrO_2$, we have the *chromites* in which chromium is also trivalent, but appears in the negative ion. Corresponding to chromium trioxide, CrO_3, and the water solution of CrO_3, which we call *chromic acid*, H_2CrO_4, we have the *chromates* in which chromium is in the negative ion and has a valence of VI. Corresponding to perchromic acid, $H_2Cr_2O_8$, several *perchromates* are known, which are unstable at ordinary temperature. Chromous compounds are not stable in air, passing readily into the higher condition of oxidation of chromic compounds.

Chromous Compounds. *Of the chromous compounds, chromous chloride and chromous hydroxide are representative and typical.*



$\mathrm{Cr}<^{\mathrm{Cl}}_{\mathrm{Cl}}$

Chromous chloride, $CrCl_2$, a white, crystalline powder, is obtained by acting upon chromium with hydrochloric acid out of contact with air.

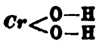
$$Cr + 2\,HCl = CrCl_2 + H_2$$

It volatilizes without decomposition, and at from 1300° to 1600° the vapor shows a specific gravity corresponding to a mixture of $CrCl_2$ and Cr_2Cl_4. It gives with water a blue solution turning green by oxidation with formation of chromic chloride,

$$4\,CrCl_2 + O_2 + 4\,HCl = 4\,CrCl_3 + 2\,H_2O$$

which, in presence of hydrochloric acid, may be reduced to chromous chloride by zinc or by the nascent hydrogen produced in the action of zinc upon the acid.

$$2\,CrCl_3 + Zn = 2\,CrCl_2 + ZnCl_2$$
$$2\,CrCl_3 + H_2 = 2\,CrCl_2 + 2\,HCl$$



$$Cr<\begin{matrix}O-H\\O-H\end{matrix}$$

Chromous hydroxide, $Cr(OH)_2$, yellow, easily oxidizable, is precipitated when sodium hydroxide or other alkali hydroxide is added to a solution of chromous chloride.

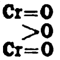
$$CrCl_2 + 2\,NaOH = \mathbf{Cr(OH)_2} + 2\,NaCl$$

When chromous hydroxide, $Cr(OH)_2$, is heated, the chromium-ion, instead of forming the oxide CrO, is oxidized at the expense of the water, assuming a higher valence, hydrogen being liberated.

$$2\,Cr(OH)_2 = Cr_2O_3 + H_2 + H_2O$$

Chromic Compounds.

Of the chromic compounds, chromic oxide, chromic hydroxide, chromic chloride, and chromic sulphate are typical.



$$\begin{matrix}Cr=O\\ \quad >O\\ Cr=O\end{matrix}$$

Chromic oxide, Cr_2O_3, may be conveniently prepared as a green amorphous powder by heating chromium trioxide, CrO_3, as already shown, or by heating ammonium dichromate, $(NH_4)_2Cr_2O_7$, obtained by dissolving chromium trioxide in water and adding ammonium hydroxide in suitable amount.

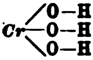
$$(NH_4)_2Cr_2O_7 = Cr_2O_3 + 4\,H_2O + N_2$$

Chromic oxide is formed as black hexagonal crystals when chromyl chloride, CrO_2Cl_2, is passed through a red-hot tube.

$$4\,CrO_2Cl_2 = 2\,Cr_2O_3 + 4\,Cl_2 + O_2$$

After ignition it is generally insoluble in acids, but is attacked by hot concentrated sulphuric acid. Chromic oxide dissolves in fused silicates or borates, and is employed to impart a green color to glass and porcelain. Ignited in mixture with alkali hydroxides or carbonates in contact with air it forms chromates.

Chromic oxide does not combine directly with water, but the corresponding chromic hydroxide may be obtained by precipitation from solutions of chromic salts.



Chromic hydroxide, $Cr(OH)_3$, may be precipitated by th addition of ammonium hydroxide, NH_4OH, to a solution of chromic chloride, $CrCl_3$.

$$CrCl_3 + 3\,NH_4OH = \mathbf{Cr(OH)_3} + 3\,NH_4Cl$$

The precipitate is grayish green in color, when formed from the gree solutions of chromic salts; from solutions of violet chromic salts it is bluish gray in color. When precipitated it retains more water than corresponds to the symbol of the simple hydroxide, and is the hydrogel $Cr(OH)_3 \cdot nH_2O$, but in a vacuum water is lost, leaving $Cr(OH)_3$.

When chromic hydroxide is heated to 200°, the insoluble *chro oxyhydroxide*, CrO(OH) (chromous acid), corresponding in composition to the *chromites*, is formed. The freshly precipitated hydro of chromic hydroxide dissolves in a solution of chromic chloride, and such a solution when dialyzed allows chromic chloride to pass the dialyzer, leaving the hydrosol of chromic hydroxide, which may be converted to the hydrogel and precipitated by addition of alkali salts.

K—O—Cr=O

Chromic hydroxide is acted upon slightly by ammoni hydroxide, forming a violet solution from which it is precipitated on boiling; and with sodium hydroxide or potassium hydrox it forms soluble *sodium chromite*, $NaCrO_2$, or *potassium chromite*, $KCrO_2$ respectively.

$$Cr(OH)_3 + KOH = KCrO_2 + 2\,H_2O$$

On boiling the solution of an alkali chromite, a precipitate is formed consisting largely of chromic hydroxide, but still holding some of the alkali element in combination. The mineral *chromite* may be regard as essentially an insoluble *ferrous chromite*, $Fe(CrO_2)_2$.

Chromic chloride, $CrCl_3$, is obtained in green solution acting upon chromic hydroxide with hydrochlor acid.

$$Cr(OH)_3 + 3\,HCl = CrCl_3 + 3\,H_2O$$

This solution, when evaporated sufficiently, deposits green deliquesce crystals of hydrous chromic chloride, $CrCl_3 \cdot 6\,H_2O$, and these, whe heated in an atmosphere of hydrogen chloride, form the anhydro chromic chloride, $CrCl_3$, as a reddish violet residue which dissolves i water to form a green solution.

A similar solution may be obtained by heating chromium trioxide, CrO_3, with concentrated hydrochloric acid,

$$2\,CrO_3 + 12\,HCl = 2\,CrCl_3 + 6\,H_2O + 3\,Cl_2$$

and this process is aided by the presence of a reducing agent, such as alcohol.

$$2\,CrO_3 + 6\,HCl + 3\,C_2H_5OH = 2\,CrCl_3 + 6\,H_2O + 3\,C_2H_4O$$

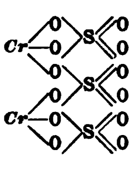
It is a curious fact that when cold green solutions of chromic chloride are treated with silver nitrate, silver chloride is formed in amount corresponding to only one third of the chlorine present in the chloride, the remaining two thirds being apparently a constituent of a complex ion which does not exchange chlorine for the NO_3-ion of silver nitrate,—a condition which might be represented by writing the symbol of the dissolved salt, $(CrCl_2)Cl$, and that of the crystallized green salt, $(CrCl_2)Cl \cdot 6\,H_2O$, which expresses simply a constitution and condition which may in reality be of considerable complexity.

On the other hand, it is possible to prepare a violet solution of chromic chloride by treating a cold solution of violet chromic sulphate with barium chloride,

$$Cr_2(SO_4)_3 + 3\,BaCl_2 = 2\,CrCl_3 + 3\,BaSO_4$$

and the precipitate obtained by acting with silver nitrate upon the solution of chromic chloride thus prepared contains all the chlorine. Upon boiling, the violet solution becomes green, and then silver nitrate forms a precipitate containing only two thirds of the chlorine. The chromic chloride in the violet solution may, therefore, be best represented by the ordinary symbol, $CrCl_3$.

When the soluble reddish violet anhydrous chromic chloride, $CrCl_3$, is heated sufficiently, it sublimes with formation of lustrous reddish violet leaflets, which dissolve in water and form the green solution only upon long boiling, or after the addition or formation of a trifling amount of chromous chloride, $CrCl_2$, which appears to act as a catalyzer. This phenomenon points to greater complexity of constitution in the anhydrous chromic chloride than would be indicated by the symbol $CrCl_3$.



Chromic sulphate, $Cr_2(SO_4)_3$, is formed in green solution when chromic hydroxide is acted upon by concentrated sulphuric acid. The solution, after standing, deposits violet crystals of hydrous chromic sulphate, $Cr_2(SO_4)_3 \cdot 15\,H_2O$, which dissolve in cold water to form a violet solution.

The violet solution of chromic sulphate is acted upon by barium chloride with formation of a violet solution of chromic chloride, and a precipitate of barium sulphate containing all the SO_4-ion of the original chromic sulphate.

Upon boiling the violet solution of chromic sulphate, a green solution is formed, from which, by the action of barium chloride, a precipitate is formed containing only one third of the SO_4-ion of the original chromic sulphate. After long standing the solution again becomes violet, when the metathesis between the chromic sulphate and barium chloride is complete. The transition of the violet chromic sulphate to the green chromic sulphate has been attributed to hydrolytic decomposition with formation of a compound containing a complex ion, $Cr_4O(SO_4)_4$, from which the SO_4-ion is not replaceable by hydrolysis.

$$\underset{\text{violet}}{2\,Cr_2(SO_4)_3} + H_2O = \underset{\text{green}}{[Cr_4O(SO_4)_4]SO_4} + H_2SO_4$$

Chromic sulphate forms double salts with the alkali sulphates which are known as the *chrome alums*. *Potassium chromium sulphate*, $KCr(SO_4)_2 \cdot 12\,H_2O$ (chrome alum), is formed as dark violet octahedra when a solution containing chromic sulphate and potassium sulphate is allowed to evaporate spontaneously. It is most conveniently prepared by acting upon potassium dichromate with sulphuric acid and a reducer such as alcohol or sulphur dioxide.

$$K_2Cr_2O_7 + H_2SO_4 + 3\,SO_2 = K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$
$$K_2SO_4 + Cr_2(SO_4)_3 + 24\,H_2O = 2\,[KCr(SO_4)_2 \cdot 12\,H_2O]$$

Sodium chromium sulphate, $NaCr(SO_4)_2 \cdot 12\,H_2O$, and *ammonium chromium sulphate*, $NH_4Cr(SO_4)_2 \cdot 12\,H_2O$, are formed similarly. All dissolve in cold water to form violet solutions, but such solutions, when heated, turn green after the fashion of the simple chromic sulphate.

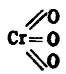
Other chromic salts possess characteristics like those of the chloride and the sulphate.

Chromates and Chromic Acid. *Corresponding to chromic oxide we have the chromates, such as potassium chromate and barium chromate, and the acid, chromic acid.*

When chromic oxide, Cr_2O_3, is heated with sodium hydroxide or sodium carbonate in presence of air, *sodium chromate*, Na_2CrO_4, is formed.

$$2\,Cr_2O_3 + 4\,Na_2CO_3 + 3\,O_2 = 4\,Na_2CrO_4 + 4\,CO_2$$

On the practical scale, the mineral *chromite*, $FeCr_2O_4$, forms the natural source from which to prepare the chromates, as well as the other chromium compounds; and the process of preparing successively *sodium chromate*, Na_2CrO_4, *sodium dichromate*, $Na_2Cr_2O_7$, and the comparatively insoluble and easily crystallizable *potassium dichromate*, $K_2Cr_2O_7$, which being easily obtained in a state of purity may be conveniently used for the preparation of the compounds of chromium, has been already described.



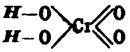
Chromium trioxide, CrO_3 (chromic anhydride), crystallizing in long red needles, is obtained, as we have seen, when concentrated sulphuric acid is added to a cold concentrated solution of potassium dichromate.

$$2\ H_2SO_4 + K_2Cr_2O_7 = 2\ KHSO_4 + 2\ CrO_3 + H_2O$$

It may be purified by washing on asbestos with concentrated nitric acid and drying in a current of air at a temperature of 60° to 80°. When heated, chromium trioxide volatilizes slightly, melts at 180°, and decomposes at 250°, evolving oxygen and leaving chromic oxide, Cr_2O_3. At ordinary temperatures it yields oxygen to oxidizable substances, igniting alcohol and even ammonia.

Concentrated hydrochloric acid and chromium trioxide react with formation of chromic chloride and liberation of chlorine.

$$2\ CrO_3 + 12\ HCl = 2\ CrCl_3 + 6\ H_2O + 3\ Cl_2$$



Chromium trioxide is readily soluble in water forming a solution possessed of acidic properties, and it may be recovered again from the solution by evaporating the water. Though the combination with water is loose and unstable, it is convenient to consider it to be a solution of *chromic acid*, H_2CrO_4, analogous to the solutions of the unstable carbonic acid and sulphurous acid.

Chromic acid has strong oxidizing capacity, acting upon sulphurous acid with formation of chromic sulphate and water,

$$2\ H_2CrO_4 + 3\ H_2SO_3 = Cr_2(SO_4)_3 + 5\ H_2O$$

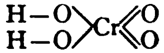
acting upon hydrogen sulphide to form chromic oxide, water, and sulphur,

$$2\ H_2CrO_4 + 3\ H_2S = Cr_2O_3 + 5\ H_2O + S$$

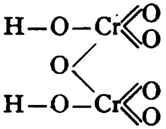
and oxidizing alcohol to aldehyde, a chromic salt being formed if an acid is present.

$$2\ H_2CrO_4 + 3\ C_2H_5OH + 3\ H_2SO_4 = C_2H_4O + Cr_2(SO_4)_3 + 8\ H_2O$$

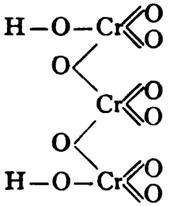
When the solution of chromic acid is treated with an alkali hydroxide, chromates are formed which vary in composition according to the proportions of the reagents. Thus, well-defined potassium chromates may be formed, which are represented by the symbols K_2CrO_4, $K_2Cr_2O_7$, $K_2Cr_3O_{10}$, which correspond respectively to *chromic acid*,



and to the *polychromic acids*,



and



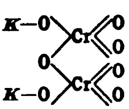
none of which, however, has ever been isolated. All solutions of chromic acid yield upon evaporation water and chromium trioxide.

Potassium chromate, K_2CrO_4, is obtained in yellow crystals when a mixture of chromic acid and potassium hydroxide in suitable amount is evaporated,

$$2\,KOH + H_2CrO_4 = K_2CrO_4 + 2\,H_2O$$

or when potassium hydroxide is added to a solution of potassium dichromate,

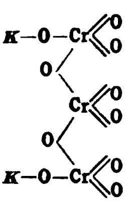
$$2\,KOH + K_2Cr_2O_7 = 2\,K_2CrO_4 + H_2O$$



Potassium dichromate, $K_2Cr_2O_7$, crystallizing from solution in large, red, triclinic prisms, fairly soluble in water, is formed when chromic acid is added to a solution of potassium chromate, or when sulphuric acid or any other suitable acid is added in proper proportion to a solution of potassium chromate.

$$K_2CrO_4 + H_2CrO_4 = K_2Cr_2O_7 + H_2O$$

$$2\,K_2CrO_4 + H_2SO_4 = K_2SO_4 + K_2Cr_2O_7 + H_2O$$



Potassium trichromate, $K_2Cr_3O_{10}$, crystallizing in dark red prisms, may be formed in similar manner from potassium chromate, or from potassium dichromate, by the action of a suitable amount of acid.

The *polychromates* are all converted to chromates by the action of a suitable amount of alkali hydroxide, the change being marked by the transition of color from the red of the polychromates to the yellow of the chromates. The reverse change from chromate to polychromate, upon addition of an acid, is similarly indicated by the change from yellow to red.

Other soluble chromates are *sodium chromate*, $Na_2CrO_4 \cdot 10\ H_2O$, and *sodium dichromate*, $Na_2Cr_2O_7 \cdot 2\ H_2O$.

Insoluble Chromates. The insoluble *barium chromate*, $BaCrO_4$, and the insoluble *lead chromate*, $PbCrO_4$ (chrome yellow), are typical of chromates which may be obtained by adding soluble chromates to soluble salts of certain elements.

$$BaCl_2 + K_2CrO_4 = \mathbf{BaCrO_4} + 2\ KCl$$
$$Pb(C_2H_3O_2)_2 + K_2CrO_4 = \mathbf{PbCrO_4} + 2\ K(C_2H_3O_2)$$

Such chromates are likewise precipitated by the action of soluble dichromates upon suitable salts. Thus, potassium dichromate may be used to precipitate lead chromate, chromic acid being formed in solution.

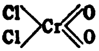
$$Pb(C_2H_3O_2)_2 + K_2Cr_2O_7 + H_2O = \mathbf{PbCrO_4} + H_2CrO_4 + 2\ K(C_2H_3O_2)$$

The action of ammonium sulphide or of an alkali sulphide upon potassium chromate or any other chromate, or upon chromic acid in solution, is peculiar in that no sulphide is formed, but chromic hydroxide is precipitated while sulphur is set free.

$$2\ K_2CrO_4 + 3(NH_4)_2S + 8\ H_2O = 2\ \mathbf{Cr(OH)_3} + 4\ KOH + 6\ NH_4OH + 3\ S$$

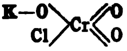
Perchromic Acid and Perchromates. Upon treating solutions of chromic acid, or solutions of chromates to which an acid has been added, with hydrogen dioxide, *perchromic acid*, $H_2Cr_2O_8$, of fine blue color, is produced in solution, and may be gathered by shaking in ether, but it decomposes with more or less rapidity. From perchromic acid have been prepared *sodium perchromate*, $Na_2Cr_2O_8$, *potassium perchromate*, $K_2Cr_2O_8$, and several similar perchromates, all unstable at ordinary temperatures.

Chlorine Derivatives. *Certain chromium compounds containing chlorine may also be formed.*



Upon heating potassium dichromate or any other chromate, or chromic acid in mixture with a chloride and sulphuric acid, a dark red volatile liquid, *chromium oxychloride* or *chromyl chloride*, CrO_2Cl_2, decomposible by water, distils.

$$CrO_2Cl_2 + 2\ H_2O = 2\ HCl + H_2CrO_4$$



Similarly by the action of hydrochloric acid upon potassium dichromate may be obtained the crystalline salt *potassium chlorchromate*, $KClCrO_3$, which may be regarded as intermediate between potassium chromate and chromyl chloride and may be made by adding chromyl chloride to a saturated solution of potassium chloride.

Summary. *Chromium is obtained by reducing with carbon or aluminium chromic oxide, which may be produced by heating chromium trioxide, formed from potassium dichromate by the action of sulphuric acid.*

Chromous chloride, formed by the action of hydrochloric acid upon chromium, may be oxidized to chromic chloride, from which chromous chloride may again be obtained by reduction with zinc or hydrogen. By acting upon chromous chloride solution with sodium hydroxide chromous hydroxide may be obtained, which gives chromic oxide when heated.

Chromic oxide may be formed by heating chromium trioxide, or ammonium chromate, or chromyl chloride.

Chromic hydroxide is formed as a precipitate from solutions of chromic salts, and yields water when heated to 200°, forming chromic oxyhydroxide, or chromous acid. Chromic hydroxide reacts with alkali hydroxides to form chromites, corresponding to chromous acid.

Chromic chloride is formed by acting upon chromic hydroxide with hydrochloric acid or by heating chromium trioxide with hydrochloric acid.

Chromic sulphate is formed by acting upon chromic hydroxide with concentrated sulphuric acid. Chromic sulphate combines with other sulphates to form double sulphates known as chrome alums.

Sodium chromate may be obtained by heating chromic oxide with sodium carbonate or sodium hydroxide, and other chromates may be similarly formed.

Chromium trioxide is formed by acting upon a dichromate, such as *potassium dichromate, with sulphuric acid. Chromium trioxide dissolves in water, forming a solution of chromic acid, which acts as a strong oxidizer.*

Potassium chromate is obtained by the interaction of potassium hydroxide and chromic acid or potassium dichromate. Potassium dichromate is formed by acting upon potassium chromate with chromic acid, or by acting upon potassium chromate with sulphuric acid. Other soluble chromates and dichromates may be formed. Barium chromate and lead chromate may be formed as precipitates.

By oxidizing chromic acid with hydrogen dioxide perchromic acid, which gives a blue color with ether, may be formed, and from it may be prepared unstable perchromates.

By the action of hydrochloric acid upon potassium dichromate, potassium chlorchromate is formed.

Molybdenum, Mo, 96.0

Molybdenum is found in combination in several rather uncommon minerals of which *molybdenite*, MoS_2, and *wulfenite*, $PbMoO_4$, are the most important. By roasting molybdenite and extracting the residue with ammonium hydroxide a solution is obtained which when evaporated leaves molybdenum trioxide, MoO_3.

Molybdenum may be obtained by passing hydrogen over molybdenum trioxide at red heat, as a silver-white metal, hard, more infusible than platinum, unchanged in air at the ordinary temperature but oxidized finally on heating to molybdenum trioxide. It is attacked by concentrated sulphuric acid and by nitric acid.

Molybdenum trioxide, MoO_3, formed when molybdenum or the mineral *molybdenite* is roasted in air, is a white mass, turning yellow on heating, fusible at red heat, insoluble in water and unaffected by acids, but acted upon by alkali hydroxides and by ammonium hydroxide.

From such solutions nitric acid separates a hydroxide $MoO(OH)_4$, which on drying gives *molybdic acid*, H_2MoO_4. Many salts of molybdic acid are known, produced by mixing molybdic acid, H_2MoO_4, or molybdenum trioxide, MoO_3, with solutions of alkali hydroxides or carbonates, or by acting upon molybdenum trioxide with these substances in a state of fusion. The *molybdates* thus produced are according to circumstances salts of molybdic acid, H_2MoO_4, or of derivative polymolybdic acids, and of these the following may serve as types: K_2MoO_4, Na_2MoO_4, $(NH_4)_2MoO_4$, $K_2Mo_3O_{10} \cdot 3\,H_2O$, $Na_2Mo_4O_{13} \cdot 6\,H_2O$, $(NH_4)_6Mo_7O_{24} \cdot 4\,H_2O$. While molybdenum trioxide, MoO_3, and molybdic acid, H_2MoO_4, are very slightly soluble in water, they are attacked by many free acids, the addition of such acids to solutions of molybdates producing either free complex acids or the salts of such complex acids. The characteristic precipitate of *ammonium phosphomolybdate*, $(NH_4)_3PO_4 \cdot 11\,MoO_3 \cdot 6\,H_2O$, obtained when sodium phosphate is added to a large excess of a solution of ammonium molybdate in nitric acid, is one of the many known complex phosphomolybdates typical of the salts of complex acids.

Mixtures of molybdic acid and other acids are affected by reducing agents. When zinc acts upon such a solution the liquid becomes blue and then passes through various stages into brown, when the composition of the molybdenum compound in the solution corresponds to that of *molybdenum sesquioxide*, Mo_2O_3, which may be obtained in anhydrous form as a black powder by reduction of molybdenum trioxide by hydrogen at red heat. Violet or copper-brown *molybdenum dioxide*, MoO_2, is obtained in the same process at a lower temperature. Between *molybdenum dioxide* and *molybdenum trioxide*, other oxides, Mo_5O_1 and Mo_3O_8, less sharply characterized, have been recognized.

Other characteristic compounds of molybdenum are the black, crystalline *molybdenum pentachloride*, $MoCl_5$; the brown, crystalline *molybdenum tetrachloride*, $MoCl_4$; the reddish brown *molybdenum trichloride*, $MoCl_3$, acted upon by concentrated sulphuric acid; the yellow *molybdenum dichloride*, $MoCl_2$; the *molybdenum oxychlorides*, $MoOCl_4$ and MoO_2Cl_2; the lower *molybdenum hydroxides*, corresponding to the chlorides; brown *molybdenum trisulphide*, MoS_3, precipitated by hydrogen sulphide from acidulated solutions of molybdates; and the black *molybdenum disulphide*, MoS_2, native as well as artificial; and the peculiar and complex *permolybdates* or *ozomolybdates*, suggestive in a degree of the persulphates, formed by the action of hydrogen dioxide upon molybdic acid and its salts.

Molybdenum appears in compounds, therefore, with valences ranging ordinarily from two to six, its commonest compounds being those in which molybdenum is sextivalent and in which it is a constituent of the negative ion.

TUNGSTEN, W, 184

Tungsten is found combined in several minerals, chief among which are *wolframite*, $(Mn, Fe)WO_4$, *scheelite*, $CaWO_4$, and *hübnerite*, $MnWO_4$. *Wolframite* fused with sodium carbonate and a little sodium nitrate is so decomposed that the cooled mass yields with water a solution of sodium tungstate, from which hydrochloric acid precipitates tungstic acid, which upon ignition changes into tungsten trioxide, WO_3.

Tungsten may be formed as a brownish black to gray powder, by the action of hydrogen upon tungsten trioxide heated to bright redness, or in massive form by igniting a mixture of tungsten trioxide and powdered aluminium, with liquid air added to accelerate combustion and elevate the temperature. It is very heavy, difficultly fusible, malleable, unchanged in air at ordinary temperatures, but burning to tungsten trioxide when sufficiently heated. It is slowly attacked by sulphuric acid, hydrochloric acid, hydrofluoric acid, or aqua regia, and a mixture of hydrofluoric acid and nitric acid attacks it vigorously. Alkali hydroxides act upon tungsten with evolution of hydrogen and formation of *tungstates*, in which sextivalent tungsten is a constituent of the negative ion.

Tungsten trioxide, WO_3, obtained from tungsten minerals, precipitated from hot solutions of tungstates by nitric acid, or produced by burning tungsten, is a yellow solid, insoluble in water, unaffected by acids, acted upon by alkali hydroxides with production of alkali *tungstates*.

From cold solutions of the tungstates, acids precipitate *tungstic acid*, H_4WO_5, or form salts of polytungstic acids. Typical tungstates are the normal *sodium tungstate*, $Na_2WO_4 \cdot 2\,H_2O$, the so-called *sodium metatungstate*, $Na_2W_4O_{13} \cdot 10\,H_2O$, and the salts, $Na_8W_{10}O_{34} \cdot 23\,H_2O$, $K_{10}W_{12}O_{41} \cdot 10\,H_2O$, and $(NH_4)_{10}W_{12}O_{41} \cdot 6\,H_2O$. Complex tungstates, salts of complex acids derived by combination of various acids with tungstic acid, are also characteristic, such as the *phosphotungstates*, $2\,Na_2O \cdot P_2O_5 \cdot 24\,WO_3 \cdot 27\,H_2O$, and $3\,(NH_4)_2O \cdot P_2O_5 \cdot 24\,WO_3 \cdot 29\,H_2O$.

Other characteristic compounds of tungsten in which the valence of tungsten is two, four, or six, are the copper-colored or brown *tungsten dioxide*, WO_2, obtained by reducing *tungsten trioxide* at dull red heat with hydrogen; the *tungsten oxychlorides*, $WOCl_4$ and WO_2Cl_2, and the *tungsten chlorides*, WCl_6, WCl_5, WCl_4, and WCl_2. The specific gravity of *tungsten hexachloride*, WCl_6, at 350° points approximately to the symbol given; at higher temperatures dissociation is marked.

Tungsten is used in the manufacture of *tungsten steel*, the addition of a small percentage of tungsten increasing much the hardness of the steel.

Uranium, U, 238.5

Uranium occurs in combination chiefly in the mineral *uraninite*, impure U_3O_8 (pitch blende), and in a few other rare minerals. Uraninite yields upon treatment with aqua regia and subsequent extraction with water a solution from which hydrogen sulphide removes impurities and leaves a solution from which, after oxidation with nitric acid, ammonium hydroxide precipitates uranic hydroxide and ferric hydroxide. Digestion of this precipitate with a hot concentrated solution of ammonium carbonate forms a solution from which, after filtering and cooling, may be crystallized *ammonium uranyl carbonate*, $2\,(NH_4)_2CO_3 \cdot UO_2CO_3$, which upon long heating at 300° yields *uranic oxide* or *uranium trioxide*, UO_3, and this when heated in hydrogen yields *uranous oxide* or *uranium dioxide*, UO_2.

Uranium, silvery white and heavy, may be obtained by reducing uranium trioxide with carbon in an electric furnace, or by reducing with sodium uranous chloride, UCl_4, obtained by heating uranium dioxide in hydrogen chloride, or by heating crude uranium with chlorine. Uranium burns in air at 170° when in fine powder, decomposes water at the ordinary temperature, combines with nitrogen at 1000° to form *uranium nitride*, and with carbon in an electric furnace to form *uranium carbide*. In its compounds uranium appears as a positive ion with a valence of IV in *uranous compounds*, and with a valence of VI, either as a positive ion or as a constituent of a negative ion, in *uranic compounds* or *uranyl compounds*, or in *uranates*.

Uranium dioxide, or *uranous oxide*, UO_2, black in color and obtained by reduction of the higher oxide with hydrogen, is acted upon by hydrochloric acid, or by concentrated sulphuric acid, with formation of green solutions. Characteristic uranous compounds, all of green tint, are *uranous sulphate*, $U(SO_4)_2 \cdot 8\,H_2O$, *uranous hydroxide*, $U(OH)_4$, and *uranous chloride*, UCl_4, obtained as shown.

In *uranic compounds* uranium and oxygen act together as a bivalent group to which the name *uranyl* is given. *Uranic oxide*, UO_3, may be obtained as a yellow powder by treating *uraninite* with nitric acid, crystallizing *uranyl nitrate*, $UO_2(NO_3)_2$, $\cdot\ 6\,H_2O$, from the solution thus obtained, and heating the uranyl nitrate to 250°. From a solution of uranyl nitrate sulphuric acid forms the less soluble and crystalline *uranyl sulphate*, $UO_2SO_4 \cdot 6\,H_2O$.

In solution the *uranyl salts* are reducible to *uranous salts* by suitable agents, while uranous salts are easily oxidized to the uranic salts.

Sodium hydroxide and potassium hydroxide act upon solutions of uranyl salts to form insoluble *sodium diuranate*, $Na_2U_2O_7$, and *potassium diuranate*, $K_2U_2O_7$, respectively, and other more complex *polyuranates* are known. So-called *peruranates*, formed by the agency of hydrogen dioxide, are known.

The so-called *uranic uranous oxide*, U_3O_8, is formed when either uranic oxide, UO_3, or uranous oxide, UO_2, is heated strongly in air, and may be regarded as a *uranous uranate*, $U(UO_4)_2$.

Many uranyl compounds show fluorescence in high degree, and the uranium glass colored with uranic oxide, UO_3, shows this effect. Uranous oxide, UO_2, stains glass and porcelain a fine black.

Uranium compounds have recently been the subject of much investigation in connection with the phenomena of *radio-activity*. The observation of Becquerel that compounds of uranium emit rays of peculiar properties has led to the discovery, by Mme. Curié, of the element *radium*, and to the announcement of other unconfirmed elements of similar character, such as *polonium* by Mme. Curié, *actinium* by Debierne, and *carolinium* by Baskerville.

CHAPTER XVII

SECONDARY SERIES—GROUP VII

Manganese, Mn, 55.0

Group VII. **Manganese.** MANGANESE occurs native in small amounts associated with iron in meteorites. It is principally found, however, in combination in minerals, from which the element may be obtained by suitable means. Manganese is a lustrous white metal, oxidized superficially in moist air, slowly decomposing boiling water, acted upon by acids with the formation of salts. Manganese forms a series oxides and hydroxides. Corresponding to the lower oxides and hydroxides we have the *manganous salts* and the *manganic salts* in which manganese is a positive ion, while corresponding to the higher oxides and hydroxides are the *manganites*, *manganates*, and *permanganates*, salts in which manganese is in the negative ion. Manganese shows a maximum valence of VII, although in some compounds it has a valence of II, III, IV, or VI.

Manganese, Mn, 55.0

Manganese Minerals. Manganese, found native in the metallic constituents of *meteorites*, occurs in combination widely distributed, and chiefly in the minerals *pyrolusite*, MnO_2, *hausmannite*, Mn_3O_4, *braunite*, Mn_2O_3, *manganite*, MnO(OH), and *rhodochrosite*, $MnCO_3$. The metal, reducible from its ores by carbon or better by aluminium, is of minor importance. It is, however, a component of various alloys, and of the iron-manganese carbides, *ferromanganese* and *spiegeleisen*, of importance in the metallurgy of Bessemer steel. The more highly oxidized compounds of manganese are useful by reason of their capacity to yield free oxygen, and indirectly to liberate the halogen elements from their compounds with metals.

Manganese. *Manganese* is separated from its oxides with difficulty by reduction with carbon, and easily by igniting the oxides with powdered aluminium. It is a slightly magnetic metal, grayish white and of brilliant luster, hard, fusible at 1900°, of specific gravity 7.2 to 8.0, readily oxidized superficially in moist air, and capable when finely divided of slowly decomposing boiling water. It is attacked by acids with formation of manganous salts, in which it appears as a positive bivalent ion.

Oxides and Hydroxides. Manganese forms compounds which may be regarded as derivatives of various oxides and hydroxides.

Manganous oxide, MnO	Manganous hydroxide, $Mn(OH)_2$
Trimanganese tetroxide, Mn_3O_4	———
Manganic oxide, Mn_2O_3	Manganic hydroxide, $Mn(OH)_3$
Manganese dioxide, MnO_2	Manganous acid, H_2MnO_3
Manganese trioxide, MnO_3	[Manganic acid, H_2MnO_4] *
Manganese heptoxide, Mn_2O_7	Permanganic acid, $HMnO_4$ †

* Represented by compounds.

† Known in solution.

Corresponding to manganous oxide, MnO, and to manganous hydroxide, $Mn(OH)_2$, are the manganous salts in which manganese is a bivalent positive ion; corresponding to manganic oxide, Mn_2O_3, and to manganic hydroxide, $Mn(OH)_3$, are possibly a few manganic salts in which manganese is a trivalent positive ion. Corresponding to manganese dioxide, MnO_2, and manganous acid, H_2MnO_3, there are a few unstable salts in which manganese is a quadrivalent positive ion, and the manganites, in which quadrivalent manganese appears in the negative ion. Corresponding to manganese trioxide, MnO_3, and to the unknown manganic acid, H_2MnO_4, are certain manganates, in which sextivalent manganese is a part of the negative ion. Corresponding to manganese heptoxide, Mn_2O_7, and to permanganic acid, $HMnO_4$, known only in solution, are the permanganates, in which septivalent manganese is a constituent of the negative ion.

Preparation of Manganous Carbonate. Metallic manganese is not a common commercial or laboratory product, and for the preparation of pure manganese salts it is usual to have recourse to the native oxides, hydroxides, or carbonates, from which crude manganese salts may be made and subsequently purified.

When the mineral *rhodochrosite*, $MgCO_3$, is treated with hydrochloric acid, crude *manganous chloride*, $MnCl_2$, is formed in solution.

$$MnCO_3 + 2\,HCl = MnCl_2 + CO_2 + H_2O$$

Crude manganous chloride may be similarly formed by acting upon *pyrolusite*, MnO_2, or upon any oxide or hydroxide of manganese, with hydrochloric acid.

$$MnO_2 + 4\,HCl = MnCl_2 + 2\,H_2O + Cl_2$$

When the solution of crude manganous chloride thus prepared is treated with a relatively small amount of sodium carbonate, a precipitate is formed which consists largely of *manganous carbonate*, $MnCO_3$. If now the liquid containing the precipitate in suspension is boiled, many of the salts which contaminate the manganous chloride, such as aluminium chloride, chromic chloride, ferric chloride, and others, react with the manganous carbonate to form precipitates of the corresponding hydroxides, which may be removed by filtration. In the solution thus obtained, ammonium sulphide forms a precipitate of manganous sulphide and other sulphides, and this when treated with dilute hydrochloric acid forms manganous chloride, leaving behind other insoluble sulphides, such as the sulphides of copper, nickel, or cobalt, if they are present.

Filtered from this precipitate, and boiled to expel hydrogen sulphide, the solution of manganous chloride yields, when treated with sodium carbonate, pure manganous carbonate,

$$MnCl_2 + Na_2CO_3 = MnCO_3 + 2\,NaCl$$

which when washed free from sodium chloride and excess of sodium carbonate may serve as a starting point for the preparation of pure manganese salts.

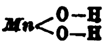
Manganous Compounds. *Of the manganous compounds manganous oxide, manganous hydroxide, manganous chloride, manganous sulphate, manganous nitrate, manganous carbonate, and manganous sulphide are typical.*

Mn=O *Manganous oxide*, MnO, greenish and amorphous, is produced when manganous carbonate is heated out of contact with air.

$$MnCO_3 = MnO + CO_2$$

It is also produced when manganese dioxide or any other high oxide of manganese is heated in hydrogen.

$$MnO_2 + H_2 = MnO + H_2O$$



$Mn\begin{smallmatrix}<O-H\\ \;\;O-H\end{smallmatrix}$

Manganous hydroxide, $Mn(OH)_2$, voluminous and white, is precipitated when sodium hydroxide or other alkali hydroxide is added to a solution of manganous chloride, or other manganous salt.

$$MnCl_2 + 2\,NaOH = \mathbf{Mn(OH)_2} + 2\,NaCl$$

Ammonium hydroxide produces partial precipitation of manganous hydroxide from solutions of manganous salts, but the presence of a sufficient amount of ammonium salt prevents the reaction, which is reversible and in equilibrium when the manganous salt and ammonium hydroxide are the only reagents originally present.

$$MnCl_2 + 2\,NH_4OH \rightleftharpoons Mn(OH)_2 + 2\,NH_4Cl$$

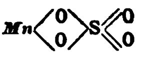
Manganous hydroxide oxidizes rapidly when exposed to air with formation of brown manganic hydroxide, $Mn(OH)_3$.

$Mn\begin{smallmatrix}<Cl\\ \;\;Cl\end{smallmatrix}$

Manganous chloride, $MnCl_2$, is obtained in solution when manganous carbonate is acted upon by hydrochloric acid.

$$MnCO_3 + HCl = MnCl_2 + H_2O + CO_2$$

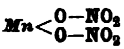
From the solution the hydrated manganous chloride, $MnCl_2 \cdot 4\,H_2O$, may be obtained in rose-red crystals, which lose their water of crystallization when heated, the salt becoming partially decomposed by hydrolysis. Manganous chloride forms with ammonium chloride the double salt $MnCl_2 \cdot 2\,NH_4Cl \cdot H_2O$, which when ignited forms the anhydrous manganous chloride.



Manganous sulphate, $MnSO_4$, is obtained in solution by acting with dilute sulphuric acid upon manganous carbonate.

$$MnCO_3 + H_2SO_4 = MnSO_4 + H_2O + CO_2$$

It crystallizes below 6° as $MnSO_4 \cdot 7\,H_2O$, at the ordinary air temperature as $MnSO_4 \cdot 5\,H_2O$, and above 25° as $MnSO_4 \cdot 4\,H_2O$. Upon heating the hydrous manganous sulphates to a moderately high temperature, $MnSO_4 \cdot H_2O$ is formed, which is stable until a temperature of 280° is reached. Manganous sulphate forms double sulphates with alkali sulphates, such as $MnSO_4 \cdot K_2SO_4 \cdot 6\,H_2O$.

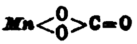


$Mn<^{O-NO_2}_{O-NO_2}$

Manganous nitrate, $Mn(NO_3)_2$, is produced when dilute nitric acid acts upon manganous carbonate.

$$MnCO_3 + 2\ HNO_3 = Mn(NO_3)_2 + H_2O + CO_2$$

From the solution containing nitric acid concentrated by evaporation at the ordinary temperature the hydrous manganous nitrate, $Mn(NO_3)_2 \cdot 6\ H_2O$, may be separated as colorless crystals, deliquescing in air, melting at a moderate temperature, and decomposing at higher temperatures with formation of nitrogen tetroxide and manganese dioxide.



$Mn<^{O}_{O}>C=O$

Manganous carbonate, $MnCO_3$, found native as the mineral *rhodochrosite*, is precipitated as a white powder when ammonium carbonate or an alkali carbonate is added to a solution of a manganous salt. It may be preserved for some time unchanged under water and out of contact with the air, turning brown by oxidation when exposed to air.

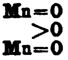
$$MnCl_2 + (NH_4)_2CO_3 = \mathbf{MnCO_3} + 2\ NH_4Cl$$

$Mn=S$ *Manganous sulphide*, MnS, is formed as a finely divided pink precipitate when ammonium sulphide or an alkali sulphide is added to a solution of manganous chloride or other manganous salt, and as a green precipitate when the manganous salt is added to a boiling solution of ammonium sulphide.

$$MnCl_2 + (NH_4)_2S = \mathbf{MnS} + 2\ NH_4Cl$$

A gray hydrous manganous sulphide, $3\ MnS \cdot H_2O$, is also sometimes formed. Manganous sulphide is acted upon by acids and is formed only incompletely or not at all when hydrogen sulphide is passed into solutions of manganous salts.

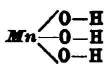
Manganic Compounds. *Of the manganic compounds, manganic oxide, manganic hydroxide, manganic sulphate, and unstable manganic chloride are typical.*



$^{Mn=O}_{Mn=O}>O$

Manganic oxide, Mn_2O_3, occurs as *braunite* in dark brown crystals, and may be obtained as a brown or black powder by igniting manganese dioxide or other oxides of manganese to redness in air or oxygen, or by heating the artificially prepared manganic hydroxide, or the native *manganite*, (MnO)OH.

$$4\ MnO_2 = 2\ Mn_2O_3 + O_2$$



Manganic hydroxide, $Mn(OH)_3$, is formed by the action of the air upon a solution of manganous chloride, ammonium chloride, and ammonium hydroxide.

$$4\,MnCl_2 + 8\,NH_4OH + 2\,H_2O + O_2 = 4\,\mathbf{Mn(OH)_3} + 8\,NH_4Cl$$

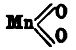
Derived oxyhydroxides are represented by the mineral *manganite*, $(MnO)OH$.

Unstable Manganic Salts.

Treated with appropriate acids, manganese hydroxide apparently forms a few unstable and easily hydrolyzed salts; with cold hydrochloric acid a brown solution is obtained which may contain the unstable *manganic chloride* or *manganese trichloride*, $MnCl_3$; with sulphuric acid a dark green liquid results, from which may be separated *manganic sulphate*, $Mn_2(SO_4)_3$, deliquescing in ordinary air to a violet solution with immediate hydrolysis to manganic hydroxide and sulphuric acid; and with hydrofluoric acid is obtained a dark red solution of *manganic fluoride* or *manganese trifluoride*, MnF_3, the least easily hydrolyzed of the manganic salts, crystallizing in dark red crystals, and forming double salts such as $2\,KF \cdot MnF_3 \cdot 2\,H_2O$.

Manganese Dioxide, Manganous Acid; Manganates.

Of the compounds of quadrivalent manganese, manganese dioxide, manganous acid, and calcium manganite are typical.



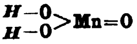
Manganese dioxide, MnO_2 (manganese peroxide), occurs as the commonest of manganese minerals, *pyrolusite*, in dark masses or in black crystals, and may be made by heating manganous nitrate to about 160°.

$$Mn(NO_3)_2 = MnO_2 + 2\,NO_2$$

Manganese dioxide is not acted upon by nitric acid. Concentrated sulphuric acid acts upon it to form *manganic sulphate*, $Mn_2(SO_4)_3$, and oxygen. Manganese dioxide is acted upon by hydrochloric acid with formation of manganous chloride, and evolution of chlorine under ordinary conditions. It is probable that at low temperatures *manganese tetrachloride*, $MnCl_4$, may be formed in this manner.

$$MnO_2 + 4\,HCl = MnCl_2 + Cl_2 + 2\,H_2O$$

Although this reaction has been largely used in the past for the production of chlorine for industrial purposes, it is at present somewhat displaced by electrolytic methods.



$$\begin{matrix} H-O \\ H-O \end{matrix}\!>Mn=O$$

Manganous acid, H_2MnO_3 (hydrated manganese dioxide), is obtained when sodium hypochlorite is added to a solution of manganous sulphate or other manganous salt, and by many other reactions in which a suitable oxidizing agent acts upon a manganous salt.

$$MnSO_4 + NaClO + 2\,H_2O = \mathbf{H_2MnO_3} + NaCl + H_2SO_4$$

It possesses acidic properties and enters into action with other substances forming *manganites.*

Upon the formation of a manganite depends the regeneration of oxidizing power in the residues from the manufacture of chlorine by the Weldon process. When to the solution of manganous chloride remaining after the action of hydrochloric acid upon manganese dioxide, milk of lime is added, and air is forced through the warmed mixture, *calcium manganite*, $CaMnO_3$, is precipitated as a black mud which may be settled out of the liquid.

$$2\,MnCl_2 + 2\,Ca(OH)_2 + 2\,O_2 = 2\,CaMnO_3 + 2\,CaCl_2 + 2\,H_2O$$

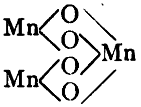
When the calcium manganite is treated with hydrochloric acid, chlorine is evolved, and the remaining solution contains manganous chloride, which may be used as before.

$$CaMnO_3 + 6\,HCl = CaCl_2 + MnCl_2 + 3\,H_2O + Cl_2$$

Mn_3O_4 *Trimanganese tetroxide*, Mn_3O_4, occurs crystallized as the mineral *hausmannite*, and may be obtained as a dark brown powder or reddish brown powder, according to conditions, by strong ignition of manganese dioxide or other oxide of manganese.

$$3\,MnO_2 = Mn_3O_4 + O_2$$

It may be regarded as *manganous manganite* of the type

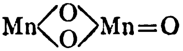


a view which gains confirmation in the fact that this oxide when treated with dilute sulphuric acid forms one equivalent of manganese dioxide to two equivalents of manganous sulphate.

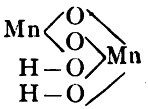
$$Mn_3O_4 + 2\,H_2SO_4 = 2\,MnSO_4 + MnO_2 + 2\,H_2O$$

Mn_2O_3

Manganic oxide, Mn_2O_3, may likewise be represented as a *manganous manganite* of the type

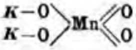


Upon this plan the native manganese hydroxide, ***manganite***, might be represented by the symbol



Manganates.

Compounds in which manganese is sextivalent are represented by the manganates, such as potassium manganate.



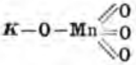
Potassium manganate, K_2MnO_4, corresponding to the hypothetical *manganic acid*, H_2MnO_4, is produced by heating manganese dioxide or other compound of manganese with potassium carbonate and potassium chlorate or other suitable oxidizing agent. When the cooled mass left after fusion is treated with cold water, a green solution is produced from which, upon evaporation under diminished pressure, potassium manganate separates in dark green crystals.

$$3\,MnO_2 + 3\,K_2CO_3 + KClO_3 = 3\,K_2MnO_4 + KCl + 3\,CO_2$$

Potassium hydroxide and potassium carbonate are without effect upon potassium manganate in solution, but the change to dark red follows the addition of an acid, or even long boiling, and back again to green when the red solution is treated with concentrated potassium hydroxide. has given to potassium manganate the name "chameleon mineral."

Permanganates; Manganese Heptoxide.

Of compounds in which the valence of manganese is taken as seven potassium permanganate and manganese heptoxide are types.



Potassium permanganate, $KMnO_4$, is formed in solution when potassium manganate is acted upon by sulphuric acid, or other suitable acid.

$$3\,K_2MnO_4 + 2\,H_2SO_4 = 2\,KMnO_4 + H_2MnO_3 + 2\,K_2SO_4 + H_2O$$

A similar effect is produced by hydrolysis when a water solution of potassium manganate is boiled.

$$3\,K_2MnO_4 + 2\,H_2O = 2\,KMnO_4 + MnO_2 + 4\,KOH$$

By the action of chlorine upon potassium manganate a still larger amount of potassium permanganate is formed,

$$2\ K_2MnO_4 + Cl_2 = 2\ KMnO_4 + 2\ KCl$$

and ozone acts similarly upon potassium manganate.

$$2\ K_2MnO_4 + O_3 + H_2O = 2\ KMnO_4 + 2\ KOH + O_2$$

Potassium permanganate, $KMnO_4$, fairly soluble and easily obtained in the form of dark red crystals, is a strong oxidizer and is valuable as a disinfectant. Potassium permanganate will act upon sulphurous acid to form manganous sulphate, potassium sulphate, sulphuric acid, and water,

$$5\ H_2SO_3 + 2\ KMnO_4 = 2\ MnSO_4 + K_2SO_4 + 2\ H_2SO_4 + 3\ H_2O$$

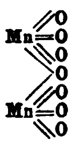
and upon ferrous sulphate in presence of sulphuric acid, to form manganous sulphate, ferric sulphate, potassium sulphate, and water.

$$10\ FeSO_4 + 2\ KMnO_4 + 8\ H_2SO_4 = 2\ MnSO_4 + 5\ Fe_2(SO_4)_3 + K_2SO_4 + 8\ H_2O$$

The reaction of potassium permanganate upon neutral salts in solutions containing an alkali hydroxide or alkali carbonate does not proceed so far, manganous acid instead of manganous sulphate being largely an end product. This is the case, too, in the curious reaction which takes place when potassium permanganate acts upon a dilute solution of manganous sulphate or other manganous salt.

$$3\ MnSO_4 + 2\ KMnO_4 + 7\ H_2O = 5\ H_2MnO_3 + K_2SO_4 + 2\ H_2SO_4$$

Permanganic acid, $HMnO_4$, is formed in solution by interaction of permanganates with acids.



Manganese heptoxide, Mn_2O_7, is separated as a dark, oily liquid when very cold concentrated sulphuric acid is added to dry potassium permanganate. On warming, dark violet vapors form which when heated are explosive. Mere contact with oxidizable material frequently decomposes manganese heptoxide, with flame if the oxidizable material is inflammable.

Compounds of manganese find extended use: the metal in alloys and in *ferromanganese* or *spiegeleisen*; manganese dioxide in the preparation of chlorine, in glass manufacture, to counteract the color of ferrous compounds, and in electrical cells, such as the Leclanché cell; permanganates as oxidizers and disinfectants.

Summary. *Manganese is separated from the native manganese oxides by reduction with carbon or powdered aluminium. By acting upon native manganese carbonate or manganese dioxide with hydrochloric acid, manganous chloride is formed, which may be purified by appropriate means, and used as a source of manganese compounds.*

Manganous oxide is made by heating manganous carbonate out of contact with air, or by reducing manganese dioxide with hydrogen. Manganous hydroxide is precipitated when a soluble hydroxide is added to a solution of manganous chloride. Manganous chloride is obtained by acting upon manganous carbonate with hydrochloric acid. Manganous sulphate is obtained by acting upon manganous carbonate with dilute sulphuric acid. Manganous nitrate is produced by the action of dilute nitric acid upon manganous carbonate. Manganous carbonate is found native. Manganous sulphide is precipitated when ammonium sulphide or an alkali sulphide acts upon manganous chloride, or other manganous salt in solution.

Manganic oxide is obtained by heating manganese dioxide or manganic hydroxide in air or oxygen. Manganic hydroxide is obtained by the action of air upon a solution of manganous chloride, ammonium chloride, and ammonium hydroxide. By the action upon manganic hydroxides of appropriate acids, unstable and easily hydrolyzed manganic salts, such as manganic chloride, manganic sulphate, and manganic fluoride, may be obtained.

Manganese dioxide is found native, and may be made by heating manganous nitrate. It is attacked by acids, with formation generally of manganous salts. Manganous acid is formed by oxidizing manganous sulphate with sodium hypochlorite. Certain manganites, such as calcium manganite, corresponding to manganous acid, are also known.

Trimanganese tetroxide is found native, and may be made by strongly heating manganese dioxide or other manganese oxides.

Potassium manganate may be made by heating manganese dioxide with potassium carbonate and potassium chlorate or other oxidizer.

Potassium permanganate is made by acting upon potassium manganate with sulphuric acid or with boiling water, or with chlorine, and is a strong oxidizer. Manganese heptoxide is formed by the action of concentrated sulphuric acid upon potassium permanganate.

CHAPTER XVIII

SECONDARY SERIES — GROUP VIII

I. THE IRON ELEMENTS

Iron, Fe, 55.9
Nickel, Ni, 58.7
Cobalt, Co, 59.0

Group VIII. The Iron Elements. THE elements of the first subdivision of Group VIII of the secondary series, the *Iron Elements*, iron, nickel, cobalt, are bright, silvery, lustrous metals, fusible, volatile only at very high temperatures, strong, malleable, ductile, and of moderate specific gravities. Iron, as we know it in ordinary life, is "rusted" in dry air very slowly, but rapidly in moist air, while nickel and cobalt are but little affected under similar conditions.

Iron, somewhat impure as ordinarily produced, being combined with carbon, silicon, phosphorus, and sulphur in varying amounts, has a very wide industrial application in the different forms of cast iron, wrought iron, and steel. Nickel is used to plate articles of copper or iron, and in alloys.

Salts. Iron, nickel, and cobalt generally combine as positive ions, each forming oxides and hydroxides. Iron forms *ferrous salts*, corresponding to ferrous oxide, FeO, and *ferric salts*, corresponding to ferric oxide, Fe_2O_3, and salts of the one class may be readily changed into salts of the other class. Nickel and cobalt form salts, the more common of which correspond generally to the lower oxides of these elements, NiO and CoO.

The prevailing valence of iron is II in the ferrous compounds, and III in the ferric compounds, while nickel and cobalt generally show a valence of II in their salts, only rarely having a valence of III.

Occurrence of Iron. Iron is one of the most common of metals, being found native in very small amounts in meteorites and certain volcanic rocks, and combined in many abundant and widely diffused minerals, from which it has been obtained for industrial purposes since prehistoric times. Most rocks contain compounds of iron, and red and yellow soils take their color from iron compounds more or less acted upon by atmospheric agencies. Some mineral waters charged with compounds of iron are known as "chalybeate waters."

Iron Minerals. Of the many minerals of which iron is a constituent, only the richer and more easily worked are used as ores. Of these the chief are *hematite*, Fe_2O_3 (specular ore, micaceous ore), dark gray crystals, or deep red compact masses; *limonite*, $Fe_4O_3(OH)_6$, and other forms of hydrated iron oxide (brown hematite, bog iron ore), black to yellow brown; *magnetite*, Fe_3O_4 (magnetic iron ore), crystalline or massive, black or dark brown, magnetic; *franklinite*, similar to magnetite, but containing zinc and manganese; and *siderite*, $FeCO_3$ (spathic ore, ironstone), yellow to brown, with pearly luster. Another iron mineral, *pyrite*, FeS_2 (iron pyrites, fool's gold), is used in the manufacture of sulphuric acid.

In the United States the iron ore deposits are widely distributed and abundant. The red hematite ores, which are the most important, are found in the Lake Superior region, particularly in northern Michigan, in Alabama, in Missouri, and elsewhere. The limonite or brown hematite ores are found in Alabama and other Southern states. Magnetite ores are found in New York, Pennsylvania, and New Jersey, and in Michigan. The siderite ores are found associated with clays in several localities. Next to those in the United States, the greatest iron-producing regions are in Great Britain, while Germany ranks high as an iron-producing country.

The iron ores are readily reduced by heating with carbon, with formation of impure iron. Under the present conditions an iron ore deposit, to be profitably developed, must be situated near accessible sources of coal and limestone required for fluxing, or it must be so situated that the crude ore may be cheaply transported to the furnaces. The manufacture of the different varieties of iron and steel from the crude iron ores is one of the world's greatest modern industries.

Nickel and Cobalt. Nickel and cobalt are found native in small amounts in meteorites. The principal ores of nickel and cobalt are *garnierite*, a nickel magnesium silicate; *pyrrhotite*, a complex magnetic iron sulphide; and *chalcopyrite*, a sulphide of copper and iron, containing also nickel and cobalt. Other nickel minerals are *niccolite*, NiAs, and *gersdorffite*, NiAsS; while common cobalt minerals are *smaltite*, $CoAs_2$, and *cobaltite*, CoAsS. In the United States the most important mine of nickel and cobalt is in Lancaster Gap, Pennsylvania, while the principal foreign mines of these elements are in New Caledonia, where large deposits of *garnierite* occur, and in Canada, Norway, and Sweden.

Iron, Fe, 55.9

Reduction of Iron Ores. When *hematite*, Fe_2O_3, or *magnetite*, Fe_3O_4, is heated with hydrogen, water is formed and nearly pure iron is left as a residue,

$$Fe_2O_3 + 3\,H_2 = 2\,Fe + 3\,H_2O$$
$$Fe_3O_4 + 4\,H_2 = 3\,Fe + 4\,H_2O$$

and these same oxides may also be reduced by heating with carbon, carbon dioxide and iron combined with some carbon being formed.

$$2\,Fe_2O_3 + 3\,C = 4\,Fe + 3\,CO_2$$
$$Fe_3O_4 + 2\,C = 3\,Fe + 2\,CO_2$$

When *limonite* and *siderite* are heated, water and carbon dioxide respectively are removed, and iron oxides remain which may be reduced by hydrogen or carbon.

For the preparation of *pure iron*, ferric oxide, prepared pure from native compounds or from crude iron, may be reduced by hydrogen; or *electrolytic iron* may be deposited from certain solutions of salts of iron under regulated conditions of the electric current.

Iron. *Iron* is a white lustrous metal, ductile and malleable, very tenacious, of specific gravity 7.78, melting at 1800°, and vaporizing at higher temperatures. When finely divided, it exists as a gray powder. It is attracted by the magnet, but does not retain its magnetism. Iron in the ordinary compact form is not attacked by dry air, though in moist air or in water containing dissolved oxygen it becomes coated with a reddish brown "rust," of iron oxide, oxy-hydroxide, or hydroxide; but alkali hydroxides or carbonates tend to retard the process of rusting. Finely divided iron produced by reduction in hydrogen at low heat is *pyrophoric*, igniting in the air when gently warmed; but if the temperature of reduction is very high, the reduced iron is not pyrophoric.

Iron is ordinarily attacked by acids with evolution of hydrogen formation of salts. When, however, a piece of polished iron is plung for an instant into concentrated nitric acid, and then removed, it is longer acted upon by ordinary nitric acid. Iron thus treated is to be in the *passive state*, but such iron loses this peculiar property it is brought in contact with ordinary iron. Iron combines with sul and with the halogen elements, to form binary compounds.

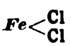
Forms of Iron. The ordinary forms of iron employed for manufact and building purposes contain, besides iron, fixed pro tions of carbon, and variable amounts of other elements, such as ph phorus, sulphur, silicon, manganese, chromium, and sometimes o metals, held in the iron in mechanical mixture, or chemically combin Ordinary pianoforte wire is one of the purer varieties of commercial i and is often employed in laboratory processes requiring nearly pure ir The proportion of carbon chiefly determines the hardness and tena and other physical characteristics, of the different varieties of ma factured iron.

Cast Iron. *Cast iron* is very brittle, and contains much as 2.3 per cent. of carbon, all chemically combine the white varieties, or partly combined and partly in the form of grap in the more common gray cast iron.

Wrought Iron and Steel. *Wrought iron* con less than 0.6 per cent. of carbon, while in *steel* the propor of carbon usually lies between 0.6 per cent. and 1.6 per ce the character of the steel, however, depending largely upon the n and proportions of the other constituents present. On account of toughness and durability iron is used more than any other metal in framework of houses and bridges, in the hulls of vessels, in railroad r in firearms, and projectiles, and in armor plate.

Iron Compounds. *Nearly all the compounds of iron are either ferrous pounds in which iron is a bivalent positive ion, or f compounds in which iron is a trivalent positive ion.*

Ferrous Compounds. *Ferrous compounds, in which iron is a bivalent p ion, are obtained by acting upon iron with other element with acids, or they may be prepared from other ferrous compoun from ferric compounds.*


$Fe<^{Cl}_{Cl}$

Ferrous chloride, $FeCl_2$, may be obtained by pas hydrogen chloride over heated iron. It is a w substance, fusible, volatilizing at red heat to form leaflets on coo possessing a specific gravity at 1300° to 1500° corresponding to its symbol, but showing at a lower temperature evidence of the existence of molecules of the composition Fe_2Cl_4.

Ferrous chloride may be formed in solution by acting upon iron with dilute hydrochloric acid, hydrogen being evolved.

$$Fe + 2\,HCl = FeCl_2 + H_2$$

Upon evaporating out of contact with the air the solution thus obtained, green crystals, deliquescent and easily oxidizable, are obtained. Upon standing in the air, a solution of ferrous chloride takes up oxygen, darkens, and ultimately a basic *ferric hydroxychloride* may be deposited. If the solution contains also hydrochloric acid, the product of the action is ferric chloride.

$$4\,FeCl_2 + 4\,HCl + O_2 = 4\,FeCl_3 + 2\,H_2O$$

Other oxidizing agents produce like effects. By nitric acid, in presence of hydrochloric acid, ferrous chloride is changed to ferric chloride, with the simultaneous formation of nitrogen dioxide, which combines with ferrous chloride to form in solution a dark brown compound, approximately $Fe_2Cl_4 \cdot NO$, broken up by heat, or by further action of nitric acid.

$$6\,FeCl_2 + 2\,HNO_3 + 6\,HCl = 6\,FeCl_3 + 4\,H_2O + 2\,NO$$

Ferrous chloride may be formed from ferric chloride by the action of suitable reducing agents, such as nascent hydrogen, zinc, iron, hydrogen sulphide, or sulphurous acid.

$$2\,FeCl_3 + H_2 = 2\,FeCl_2 + 2\,HCl$$

$$2\,FeCl_3 + Zn = 2\,FeCl_2 + ZnCl_2$$

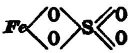
$$2\,FeCl_3 + Fe = 3\,FeCl_2$$

$$2\,FeCl_3 + H_2S = 2\,FeCl_2 + 2\,HCl + S$$

$$2\,FeCl_3 + H_2SO_3 + H_2O = 2\,FeCl_2 + 2\,HCl + H_2SO_4$$

With alkali chlorides ferrous chloride forms double salts, such as $FeCl_2 \cdot 2\,KCl \cdot 2\,H_2O$.

Ferrous sulphate, $FeSO_4$ (green vitriol, copperas), may be made by acting upon iron with dilute sulphuric acid, hydrogen being evolved in the process.



$$Fe + H_2SO_4 = FeSO_4 + H_2$$

By evaporating the solution transparent green crystals of composition $FeSO_4 \cdot 7\ H_2O$ are obtained, which lose six equivalents of water at 110°, forming white $FeSO_4 \cdot H_2O$, from which the remaining water may be removed by heating to 300°.

When ferrous sulphate in solution is exposed to air, a basic *ferric hydroxysulphate* is precipitated,

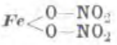
$$4\ FeSO_4 + 2\ H_2O + O_2 = 4\ \mathbf{Fe(OH)SO_4}$$

and crystallized ferrous sulphate undergoes similar change superficially in air.

Other oxidizing agents produce like effects upon ferrous sulphate. Nitric acid oxidizes ferrous sulphate, with the formation at the same time of nitrogen dioxide, which combines with ferrous sulphate, as with ferrous chloride, to form the dark brown compound $Fe_2S_2O_8 \cdot NO$ in solution, unstable and broken up by heat. This compound is produced when strong sulphuric acid is added to a strong solution of ferrous sulphate containing even a trace of nitrate, and the dark brown color thus formed serves as a delicate test for nitrates.

By mixing ferrous sulphate solution with sulphuric acid, crystals of *ferrous disulphate*, FeS_2O_7, may be obtained, readily decomposed by water. With other sulphates ferrous sulphate forms double salts, such as *Mohr's salt*, $Fe(NH_4)_2(SO_4)_2 \cdot 6\ H_2O$, and $FeK_2(SO_4)_2 \cdot 6\ H_2O$.

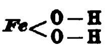
Crystallized ferrous sulphate occurs native as the mineral *melanterite*, and is found in the drainage water of some mines. It is largely manufactured by submitting *pyrite*, FeS_2, to the oxidizing influence of the atmosphere, and is also formed as a by-product of the manufacture of copper sulphate. It is used in the manufacture of ink and in dyeing.


$$Fe\begin{matrix}\diagup O-NO_2\\ \diagdown O-NO_2\end{matrix}$$

Ferrous nitrate, $Fe(NO_3)_2$, may be obtained in solution by acting upon iron with cold very dilute nitric acid, usually with formation of ammonium nitrate.

$$4\ Fe + 10\ HNO_3 = 4\ Fe(NO_3)_2 + NH_4NO_3 + 3\ H_2O$$

It may also be made by acting upon ferrous sulphate with barium nitrate, removing the precipitated barium sulphate by filtration, and evaporating the solution over sulphuric acid, when unstable crystals of the composition $Fe(NO_3)_2 \cdot 6\ H_2O$ are obtained, which are easily converted to a basic ferric nitrate.



$\mathrm{Fe}{<}\begin{matrix}\mathrm{O-H}\\ \mathrm{O-H}\end{matrix}$

Ferrous hydroxide, $Fe(OH)_2$, may be best obtained by precipitation from solutions of other ferrous salts. It is formed as a white precipitate when ammonium hydroxide is added to a solution of ferrous chloride, $FeCl_2$,

$$FeCl_2 + 2\,NH_4OH = Fe(OH)_2 + 2\,NH_4Cl$$

or when any other soluble hydroxide is added to a solution of a ferrous salt out of contact with the air. In contact with the atmosphere the precipitate, while floating in the liquid, absorbs oxygen rapidly, with corresponding change of color from white to green and finally to reddish brown, becoming changed into ferric hydroxide. Removed from the liquid and exposed to air, it is instantly oxidized.

$$4\,Fe(OH)_2 + 2\,H_2O + O_2 = 4\,Fe(OH)_3$$

Ferrous hydroxide is acted upon by acids with formation of the corresponding salts: by sulphuric acid with the formation of *ferrous sulphate*, $FeSO_4$,

$$Fe(OH)_2 + H_2SO_4 = FeSO_4 + 2\,H_2O$$

by nitric acid with formation of *ferrous nitrate*, $Fe(NO_3)_2$,

$$Fe(OH)_2 + 2\,HNO_3 = Fe(NO_3)_2 + 2\,H_2O$$

and by hydrochloric acid with formation of *ferrous chloride*, $FeCl_2$,

$$Fe(OH)_2 + 2\,HCl = FeCl_2 + 2\,H_2O$$

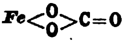
but inasmuch as ferrous hydroxide is so sensitive to the action of air, the ferrous salts prepared in this manner are never quite free from ferric salts.

$Fe{=}O$ *Ferrous oxide*, FeO, corresponding to ferrous hydroxide, may be prepared as a black powder, easily oxidized in air spontaneously or when warmed, by heating ferric oxide to 300° in hydrogen, or in a mixture of carbon monoxide with carbon dioxide under suitable conditions,

$$Fe_2O_3 + H_2 = 2\,FeO + H_2O$$

or by heating ferrous oxalate, FeC_2O_4, to 160°.

$$FeC_2O_4 = FeO + CO + CO_2$$



$\mathrm{Fe}{<}\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}{>}\mathrm{C{=}O}$

Ferrous carbonate, $FeCO_3$, occurring native as the crystalline mineral *siderite*, is precipitated, white and voluminous, but easily oxidized in the air to ferric hydroxide, $Fe(OH)_3$, when an alkali carbonate, such as sodium carbonate, is added to the solution of a ferrous salt, such as ferrous chloride.

$$FeCl_2 + Na_2CO_3 = \mathbf{FeCO_3} + 2\,NaCl$$

Fe=S *Ferrous sulphide*, FeS (iron monosulphide), falls as a black precipitate when ammonium sulphide, or an alkali sulphide, is added to the solution of a ferrous salt, such as ferrous chloride.

$$FeCl_2 + (NH_4)_2S = \mathbf{FeS} + 2\,NH_4Cl$$

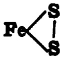
The same precipitate is formed, mixed with sulphur, when ammonium sulphide acts upon a ferric salt, such as ferric chloride.

$$2\,FeCl_3 + 3\,(NH_4)_2S = 2\,\mathbf{FeS} + \mathbf{S} + 6\,NH_4Cl$$

Ferrous sulphide is attacked by acids with evolution of hydrogen sulphide,

$$FeS + 2\,HCl = H_2S + FeCl_2$$

and this reaction is utilized in the laboratory for the production of hydrogen sulphide. The ferrous sulphide is prepared for this purpose, however, as a dark gray metallic mass, by fusing together iron and sulphur in the proper proportions.



When ferrous sulphide is gently heated with sulphur, *iron disulphide*, FeS_2, is formed as a yellow crystalline mass.

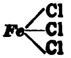
$$FeS + S = FeS_2$$

It may also be formed by passing hydrogen sulphide over ferric oxide, Fe_2O_3, or ferric chloride, $FeCl_3$, heated to redness. It is found native as the mineral *pyrite* (iron pyrites, or fool's gold), which occurs as hard, yellow cubes of specific gravity 4.95 to 5.1, and as *marcasite* (white iron pyrites), of specific gravity 4.85 to 4.9, paler in color than pyrite. Iron pyrites is largely used commercially as a source of sulphur and in the manufacture of sulphuric acid, yielding sulphur when heated out of contact with the air, and sulphur dioxide when roasted in air.

$$FeS_2 = FeS + S$$

$$4\,FeS_2 + 11\,O_2 = 2\,Fe_2O_3 + 8\,SO_2$$

Ferric Compounds. *Ferric compounds, in which iron is a trivalent positive ion, may be made by direct combination of certain elements* *with iron or with ferrous compounds, or they may be prepared from other ferric compounds, or from ferrous compounds.*



Ferric chloride, $FeCl_3$, may be obtained in anhydrous condition by passing chlorine over heated iron,

$$2\,Fe + 3\,Cl_2 = 2\,FeCl_3$$

or by passing hydrogen chloride over ferric oxide.

$2[HNO_3 + 3\,HCl] =$ aqua

$$Fe_2O_3 + 6\,HCl = 2\,FeCl_3 + 3\,H_2O$$

$6\,FeCl_2 + [2\,HNO_3 + 6\,HCl] = 6\,FeCl_3 + 4\,H_2O + 2\,NO$

The anhydrous ferric chloride boils at 280–285°, and between 320° and 440° its specific gravity corresponds to the molecular symbol Fe_2Cl_6, while between 750° and 1050° the specific gravity points to $FeCl_3$ as the molecular symbol, although at this temperature some of the molecules are dissociated into $FeCl_2$ and chlorine. The study of the effect of ferric chloride in raising the boiling points of alcohol and ether when dissolved in these respective solvents indicates that in these solutions ferric chloride has a molecular weight corresponding to the symbol $FeCl_3$.

Ferric chloride dissolves in water to a solution of brownish yellow color from which, according to conditions, yellowish or reddish crystals of hydrous ferric chlorides, $Fe_2Cl_6 \cdot 12\,H_2O$, $Fe_2Cl_6 \cdot 7\,H_2O$, $Fe_2Cl_6 \cdot 5\,H_2O$, and $Fe_2Cl_6 \cdot 4\,H_2O$ may be obtained. A similar solution and similar salts may be obtained by acting upon ferric hydroxide or ferric oxide with hydrochloric acid,

$$Fe(OH)_3 + 3\,HCl = FeCl_3 + 3\,H_2O$$
$$Fe_2O_3 + 6\,HCl = 2\,FeCl_3 + 3\,H_2O$$

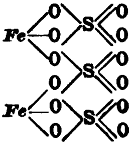
or by acting with chlorine upon ferrous chloride in solution.

$$2\,FeCl_2 + Cl_2 = 2\,FeCl_3$$

Ferric chloride in solution can act upon ferric hydroxide in varying amounts, with formation of dark-colored solutions of *ferric hydroxychlorides*. With ammonia, ferric chloride combines to form $FeCl_3 \cdot 4\,NH_3$, and with hydrogen chloride to form $FeCl_3 \cdot HCl \cdot 2\,H_2O$, and other similar compounds are known. With other chlorides it forms double salts, such as $FeCl_3 \cdot 2\,KCl \cdot H_2O$, and $FeCl_3 \cdot MgCl_2 \cdot H_2O$.

Suitable reducing agents, such as nascent hydrogen, zinc, iron, hydrogen sulphide, and sulphurous acid, reduce ferric chloride to ferrous chloride.

$$2\,FeCl_3 + H_2 = 2\,FeCl_2 + 2\,HCl$$
$$2\,FeCl_3 + Zn = 2\,FeCl_2 + ZnCl_2$$
$$2\,FeCl_3 + Fe = 3\,FeCl_2$$
$$2\,FeCl_3 + H_2S = 2\,FeCl_2 + 2\,HCl + S$$
$$2\,FeCl_3 + H_2SO_3 + H_2O = 2\,FeCl_2 + 2\,HCl + H_2SO_4$$



Ferric sulphate, $Fe_2(SO_4)_3$, left as a white mass when its reddish brown solution in water is evaporated, may be made by acting upon ferric hydroxide or ferric oxide with sulphuric acid.

$$2\,Fe(OH)_3 + 3\,H_2SO_4 = Fe_2(SO_4)_3 + 6\,H_2O$$
$$Fe_2O_3 + 3\,H_2SO_4 = Fe_2(SO_4)_3 + 3\,H_2O$$

It is conveniently produced in solution, with evolution of nitrogen dioxide, when nitric acid is added to a hot solution of ferrous sulphate containing free sulphuric acid.

$$6\,FeSO_4 + 3\,H_2SO_4 + 2\,HNO_3 = 3\,Fe_2(SO_4)_3 + 4\,H_2O + 2\,NO$$

Ferric sulphate may also be made by acting with hot concentrated sulphuric acid upon iron,

$$2\,Fe + 6\,H_2SO_4 = Fe_2(SO_4)_3 + 6\,H_2O + 3\,SO_2$$

or upon ferrous sulphate,

$$2\,FeSO_4 + 2\,H_2SO_4 = Fe_2(SO_4)_3 + 2\,H_2O + SO_2$$

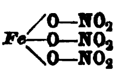
sulphur dioxide being formed in each case.

Ferric sulphate, $Fe_2(SO_4)_3$, decomposes upon being heated, forming ferric oxide and sulphur trioxide.

$$Fe_2(SO_4)_3 = Fe_2O_3 + 3\,SO_3$$

Suitable reducing agents change ferric sulphate to ferrous sulphate.

When a dilute water solution of ferric sulphate is boiled, various basic *ferric hydroxysulphates* are deposited, and similar compounds occur as rare minerals. From solutions of mixtures of ferric sulphate and other soluble sulphates, double salts of the nature of *alums* may be obtained, such as *potassium ferric alum*, $KFe(SO_4)_2 \cdot 12\,H_2O$, and *ammonium ferric alum*, $NH_4Fe(SO_4)_2 \cdot 12\,H_2O$. The double salt $FeSO_4 \cdot Fe_2(SO_4)_3 \cdot 12\,H_2O$ occurs as the mineral *roemerite*.



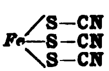
Ferric nitrate, $Fe(NO_3)_3$, may be made by heating iron with moderately dilute nitric acid, with formation of nitrogen dioxide chiefly,

$$Fe + 4\,HNO_3 = Fe(NO_3)_3 + NO + 2\,H_2O$$

or by the action of ferric hydroxide, $Fe(OH)_3$, upon nitric acid.

$$Fe(OH)_3 + 3\,HNO_3 = Fe(NO_3)_3 + 3\,H_2O$$

From the resulting solution colorless deliquescent crystals of the composition $Fe(NO_3)_3 \cdot 6\,H_2O$ may be obtained. Several basic ferric nitrates are also known. When ferric nitrate is heated, it is decomposed with formation of ferric oxide, Fe_2O_3, and evolution of nitrogen oxides.

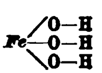


Ferric sulphocyanate, $Fe[S(CN)]_3$, in blood-red solution, is produced when potassium sulphocyanate is added to a solution of ferric chloride, $FeCl_3$, or any other ferric compound.

$$FeCl_3 + 3\,KCNS = Fe[S(CN)]_3 + 3\,KCl$$

Among the other more common ferric salts may be mentioned *ferric fluoride*, FeF_3, *ferric bromide*, $FeBr_3$, and *ferric phosphate*, $FePO_4 \cdot 2\,H_2O$.

A complex basic *ferric arsenite*, $Fe_4O_5(OH)_5As$, insoluble in water, is made by acting upon a soluble arsenite with freshly precipitated ferric hydroxide. Freshly precipitated ferric hydroxide is, for this reason, taken as an antidote against arsenic poisoning.

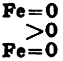


Ferric hydroxide, $Fe(OH)_3$, one of the ferric compounds prepared from other ferric compounds, is formed as a voluminous reddish brown precipitate when ammonium hydroxide is added to a solution of ferric chloride, $FeCl_3$, or when any soluble hydroxide is added to a solution of a ferric salt.

$$FeCl_3 + 3\,NH_4OH = Fe(OH)_3 + 3\,NH_4Cl$$

Although under ordinary conditions ferric hydroxide is insoluble in water, when to a precipitate suspended in water ferric chloride or ferric acetate is added, a clear solution of basic salts results, from which by dialysis a hydrosol of pure ferric hydroxide may be obtained upon the dialyzer. From the hydrosol, upon addition of a little alkali hydroxide or acid, a hydrogel of ferric hydroxide is precipitated.

A number of ferric oxyhydroxides may be produced from precipitated ferric hydroxide under various conditions of precipitation or drying, corresponding to some of which we have naturally occurring minerals. Thus we have the known series of minerals, *limnite*, $Fe_4O_{12}H_{12}$, *xanthosiderite*, $Fe_4O_{10}H_8$, *limonite*, $Fe_4O_9H_6$, *goethite*, $Fe_4O_8H_4$, *turgite*, $Fe_4O_7H_2$, representing successive stages of dehydration of the hypothetical ferric hydroxide, $Fe_4(OH)_{12}$. When ignited, ferric hydroxide and the various ferric oxyhydroxides lose water, leaving a residue of ferric oxide.



$$\begin{array}{l} Fe=O \\ \quad\;>O \\ Fe=O \end{array}$$

· *Ferric oxide*, Fe_2O_3 (iron sesquioxide), found as the mineral *hematite*, may be prepared by igniting ferric hydroxide or the ferric oxyhydroxides, and is manufactured on a large scale by strongly heating ferrous sulphate (green vitriol) and used, under the name of *rouge*, in polishing glass and metals, and as a red pigment. It is attacked with difficulty by hydrochloric acid and by nitric acid, and more readily by sulphuric acid of moderate concentration. Upon ignition in hydrogen or in carbon monoxide, it is reduced to iron.

Besides ferrous oxide and ferric oxide, to which most iron compounds correspond, there is another iron oxide, magnetic iron oxide.

Fe_3O_4

Magnetic iron oxide, Fe_3O_4, is slowly formed as a black magnetic powder by heating iron to white heat in air,

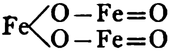
$$3\,Fe + 2\,O_2 = Fe_3O_4$$

or by passing steam over iron heated to incandescence.

$$3\,Fe + 4\,H_2O = Fe_3O_4 + 4\,H_2$$

It may also be made by heating ferrous oxide, FeO, with ferric oxide, Fe_2O_3, or in air, and is reducible by hydrogen or carbon. It is the chief constituent of the "blacksmith's scale," hammered from iron heated to incandescence. It is found as the mineral *magnetite*, or "lodestone," an important iron ore.

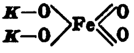
Magnetic iron oxide is attacked by acids with formation of ferrous salts and ferric salts. In composition it corresponds to a compound of ferrous oxide with ferric oxide, a *ferrous ferrite*,



$$Fe\!\left\langle\begin{array}{l} O-Fe=O \\ O-Fe=O \end{array}\right.$$

and it may be formed in hydrated condition, $Fe_3O_4 \cdot H_2O$, by adding a soluble hydroxide to a solution of a ferrous salt and a ferric salt mixed in the proper proportion.

Besides the ferrous compounds and the ferric compounds in which iron appears as a bivalent or trivalent positive ion, there are a few compounds, formed under exceptional circumstances, in which iron appears with a valence of six, as a part of the negative ion.



Potassium ferrate, K_2FeO_4, crystallizing from solution in dark red prisms, is produced when iron filings are fused with potassium nitrate, when chlorine is passed into a solution of potassium hydroxide in which ferric hydroxide is suspended, or when a mixture of ferric oxide and potassium peroxide is heated to redness. The cold water solution of potassium ferrate decomposes when heated or upon standing, with formation of ferric hydroxide, potassium hydroxide, and oxygen.

Iron Ferrocyanides and Ferricyanides.

Certain compounds in which iron enters as part of a complex ion fail to show the ordinary reaction of ferrous or ferric compounds.

Potassium ferrocyanide, $K_4[Fe(CN)_6]$, and potassium ferricyanide, $K_3[Fe(CN)_6]$, the preparation of which as cyanogen compounds has already been mentioned, show with salts of iron characteristic reactions of great practical value in distinguishing between ferrous compounds and ferric compounds.

With a ferrous salt, such as ferrous sulphate, $FeSO_4$, potassium ferrocyanide, $K_4[Fe(CN)_6]$, precipitates bluish white *potassium ferrous ferrocyanide*, $K_2Fe[Fe(CN)_6]$,

$$FeSO_4 + K_4[Fe(CN)_6] = \mathbf{K_2Fe[Fe(CN)_6]} + K_2SO_4$$

while with a ferric salt, such as ferric chloride, potassium ferrocyanide precipitates dark blue *ferric ferrocyanide*, $Fe_4[Fe(CN)_6]_3$ (Prussian blue).

$$4\,FeCl_3 + 3\,K_4[Fe(CN)_6] = \mathbf{Fe_4[Fe(CN)_6]_3} + 12\,KCl$$

On the other hand, with a ferrous salt, such as ferrous sulphate, $FeSO_4$, potassium ferricyanide, $K_3[Fe(CN)_6]$, forms a dark blue *ferrous ferricyanide*, $Fe_3[Fe(CN)_6]_2$ (Turnbull's blue),

$$3\,FeSO_4 + 2\,K_3[Fe(CN)_6] = \mathbf{Fe_3[Fe(CN)_6]_2} + 3\,K_2SO_4$$

while the effect of potassium ferricyanide, $K_3[Fe(CN)_6]_3$, upon a ferric salt, such as ferric chloride, $FeCl_3$, is to produce a solution, colored brown or green according to conditions, which may possibly contain *ferric ferricyanide*, $Fe[Fe(CN)_6]$.

Summary. *Of the ferrous compounds, ferrous chloride is made by acting upon iron with hydrochloric acid. It is changed by air into an oxychloride. It may be oxidized to ferric chloride by air, and by nitric acid in the presence of hydrochloric acid. It may be formed by reducing ferric chloride with hydrogen, zinc, iron, hydrogen sulphide, or sulphurous acid. It forms double compounds with other chlorides. Ferrous sulphate is made by acting upon iron with dilute sulphuric acid. It forms a basic ferric hydroxysulphate when its solution is exposed to air. Ferrous nitrate is made by acting upon iron with dilute nitric acid.*

Ferrous hydroxide is precipitated when ammonium hydroxide or an alkali hydroxide is added to a solution of ferrous chloride or other ferrous salt. It is oxidized by air to ferric hydroxide, and acids attack it to form ferrous salts. Ferrous oxide is made by heating ferric oxide in hydrogen, or by heating ferrous oxalate.

Ferrous carbonate is precipitated when a soluble carbonate is added to a solution of a ferrous salt. It is changed into ferric hydroxide by action of the air in presence of water.

Ferrous sulphide is precipitated when ammonium sulphide or an alkali sulphide is added to a solution of a ferrous or ferric salt. It may also be made by fusing together iron and sulphur. It is attacked by acids with formation of hydrogen sulphide. Iron disulphide is formed when ferrous sulphide and sulphur are heated together. When heated out of contact with air it yields ferrous sulphide and sulphur; and when heated in air it forms ferric oxide and sulphur dioxide.

Of the ferric compounds, ferric chloride may be made by acting upon iron with chlorine, or by acting upon ferric oxide or ferric hydroxide with hydrochloric acid, or by acting upon ferrous chloride with chlorine. It is reduced to ferrous chloride by iron, and by other reducing agents. It forms double compounds. Ferric sulphate may be made by acting upon ferric hydroxide or ferric oxide with sulphuric acid, or by oxidizing ferrous sulphate with nitric acid, or by acting upon iron or ferrous sulphate with hot concentrated sulphuric acid. Ferric sulphate is acted upon by water to form basic hydroxysulphates. With other sulphates ferric sulphate forms alums. It is decomposed by heating into ferric oxide and sulphur trioxide. It is reduced to ferrous sulphate by suitable reducing *agents. Ferric nitrate may be made by heating iron with moderately diluted nitric acid, or by acting upon ferric hydroxide with nitric acid. It is decomposed by heating, with formation of ferric oxide. Other ferric salts are ferric sulphocyanate, ferric fluoride, ferric bromide, ferric phosphate, and basic ferric arsenite.*

Ferric hydroxide may be precipitated by adding a soluble hydroxide to a solution of a ferric salt. Similar ferric oxyhydroxides may be likewise prepared. Ferric oxide is found native. It may be made by heating a ferrous salt or ferric hydroxide. It is reduced to iron by hydrogen, and is attacked by acids with some difficulty.

Magnetic iron oxide is formed by heating iron to white heat in air, or by passing steam over incandescent iron. It is attacked by acids with formation of ferrous salts and ferric salts.

Potassium ferrous ferrocyanide, ferric ferrocyanide (Prussian blue), ferrous ferricyanide (Turnbull's blue), may be formed as precipitates; ferric ferricyanide may be formed in solution.

Metallurgy of Iron.

The *metallurgy of iron* includes the reduction of crude iron ores in the *blast furnace*, and the purification of the iron by oxidation in the *puddling furnace* or *Bessemer converter* or other suitable apparatus. The product of the blast furnace is the *white* or *gray cast iron*, that of the puddling furnace is usually *wrought iron*, while the Bessemer converter produces *steel.*

The Blast Furnace.

The iron ore, with or without previous calcining or roasting, according to circumstances, is mixed with broken limestone, or other suitable *flux*, and the mixture of ore and flux is fed into the *blast furnace* in alternate layers, with coke or coal, where it is heated to incandescence in an upward current of air forced into the furnace under pressure. As a result of the heating, the iron oxide is reduced to iron, which combines with carbon, silicon, manganese, and other impurities to form at the bottom of the furnace a molten mass, which is drawn off and cast into bars or "pigs," while the lighter flux combines with the greater part of the silicates and other earthy

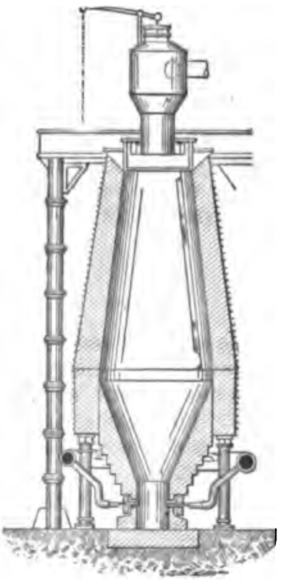


FIG. 20.—Blast Furnace.

matters in the ore to form a molten *slag*, which rests in a layer above the iron. The carbon dioxide and carbon monoxide and other furnace gases pass out at the top of the furnace.

The *blast furnace* consists of a high cylindrical stack of masonry, lined with fire brick and encased in wrought iron plates. The interior chamber usually tapers at the top and bottom. At the top is an opening to admit the charges of ore and flux, and an apparatus which serves to conduct away the hot burner gases, which may be used elsewhere as fuel. At the bottom of the furnace is a hearth, into which pass *tuyères*, or pipes, through which a blast of hot air is forced under pressure.

The reactions of the blast furnace are many and complex, and are different in different parts of the furnace. The oxygen of the hot air blast on coming in contact with the carbon forms first carbon dioxide,

$$C + O_2 = CO_2$$

which meeting with more carbon becomes carbon monoxide.

$$CO_2 + C = 2\,CO$$

In the upper regions of the furnace the ore is completely disintegrated, and the reduction of the ore by the action of carbon monoxide to ferrous oxide or to iron disseminated through the mass begins, both reactions coming to an equilibrium which limits the reducing capacity of the carbon monoxide.

$$Fe_2O_3 + CO \rightleftarrows 2\,FeO + CO_2$$

$$Fe_2O_3 + 3\,CO \rightleftarrows 2\,Fe + 3\,CO_2$$

Somewhat lower in the furnace the active expulsion of carbon dioxide from the limestone takes place, and calcium oxide is produced. Next, fusion of the mass begins and better contact of materials takes place, the reduction of the ore being completed by the action of carbon,

$$Fe_2O_3 + 3\,C = 3\,CO + 2\,Fe$$
$$FeO + C = CO + Fe$$

while a similar reducing action takes place upon the oxygen compounds of manganese, silicon, phosphorus, and other elements. The reduced iron coming into contact with the carbon combines with it and, at the same time taking up the other reduced elements, becomes a fusible mass, which is drawn off at the bottom of the furnace and cooled as *pig iron*.

The materials employed as a *flux* are chosen with reference to the composition of the ores. Limestone is employed for ores rich in silica, while ores containing lime and magnesia require a flux of sand or aluminium compounds. Blast furnace *slags* consist for the most part of double silicates of calcium and aluminium of complex composition, and are formed by the combination of the flux with the earthy impurities of the iron. On the lower contracted portion of the furnace, where the molten mass attains intense whiteness, the heavier iron settles to the bottom, and the lighter slag separates as a layer on top of the iron. Slags are sometimes run into molds to make building material or blown by steam into *glass wool* used for non-conducting packing.

Cast Iron. The *cast iron* obtained from the blast furnace usually contains from 2.3 to 5.1 per cent. of carbon, and variable proportions of silicon, phosphorus, sulphur, manganese, and other elements. Cast iron is obtained in two varieties—*white cast iron*, formed by rapid cooling, containing the carbon chemically combined; and *gray cast iron*, formed by slow cooling, containing uncombined carbon as graphite. Cast iron melts at a temperature between 1050° and 1250°, the gray iron melting more readily than the white. Gray cast iron is used for casting, while white cast iron is made into wrought iron and steel. When cast iron cools from molten condition, it expands slightly. Cast iron is very brittle, and breaks easily under a blow. Cast iron containing a large proportion of manganese and rich in carbon is known as *spiegeleisen* (mirror iron), or, when the proportion of manganese reaches 25 per cent., as *ferromanganese*. When cast iron is attacked by acids, gaseous hydrocarbons are evolved, producing a characteristic odor.

Wrought Iron. *Wrought iron* is usually made by a *puddling process* in which cast iron is melted in a reverberatory furnace lined with iron oxide ore, in which coal is burned in such a manner that the flame passes through the furnace, coming in contact with the charge of cast iron and the ore. The molten cast iron is thus subjected to the oxidizing influence of both the iron oxide and the air, and most of the carbon is burned to carbon monoxide, the silicon and other impurities being similarly changed, leaving a pasty mass of iron, containing less than 0.6 per cent. of carbon, which is removed from the furnace and hammered and rolled into useful forms of the malleable *wrought iron*.

If the oxidizing action in the puddling furnace is stopped at the proper time, before the proportion of carbon has been sufficiently reduced to form wrought iron, a variety of steel may be obtained.

Castings made of white cast iron may be made malleable by embedding them in powdered ferric oxide and exposing them for some time to red heat. the oxygen of the oxide serving to oxidize some of the carbon present in the cast iron.

Wrought iron melts at from 1900° to 2100°, but becomes soft at red heat. It is harder than cast iron, and is tough and malleable, but bends easily under strain.

The Bessemer Converter. *Steel* is usually made by melting cast iron in a large vessel of peculiar shape known as a *Bessemer converter*, and passing through the molten mass a blast of air which raises the temperature to above 2100° and oxidizes nearly all of the carbon and other impurities, leaving a residue of nearly pure iron, to which sufficient *spiegeleisen*, or *ferromanganese* is added to give the desired proportion of carbon to the mixture. If the cast iron employed contains phosphorus, a converter is employed containing a lining of clay, silica and lime, with which the phosphorus will combine with formation of a slag of calcium phosphate. For iron free from phosphorus a lining of an ordinary refractory silicate is used.

The *Bessemer converter* is a large vessel of wrought iron, peculiarly shaped, suitably lined and mounted on trunnions, and provided with openings at the bottom to admit a powerful blast of air. The converter is placed in a horizontal position and charged with molten cast iron, the air blast is started, the converter is swung into a vertical position, and the oxidation continued until the flame at the open mouth of the converter shows that the carbon has been burned out sufficiently. The converter is now tipped to the horizontal position, the required charge of spiegeleisen is added, and the blast is then continued for a few minutes, to thoroughly mix the molten mass, after which the contents are turned out into a ladle to be cast into ingots and forged.

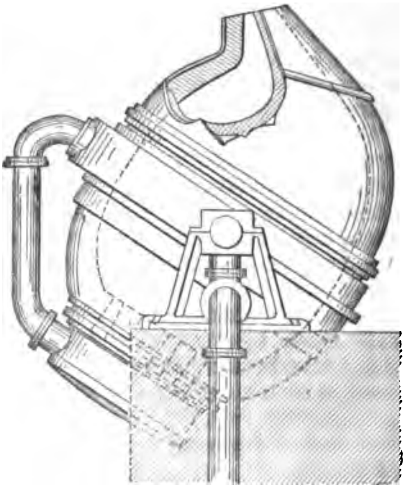


FIG. 21. — Bessemer Converter.

Steel is also made by the *Siemens-Martin* process, in which the requisite proportion of carbon is obtained by heating a mixture of cast iron and wrought iron, taken in suitable proportions, in an especially constructed *open hearth furnace*, employing gaseous fuel.

Steel may be made from wrought iron by the *cementation process*, in which iron bars are embedded in fine charcoal and subjected to red heat, when carbon penetrates the iron from the outer surface inward. Wrought iron implements are sometimes *case-hardened*, or superficially covered with steel, by heating them in contact with a carbon compound, such as potassium ferrocyanide, and then cooling them suddenly.

Steel. *Steel* usually contains from 1.6 to 0.6 or less per cent. of carbon, together with variable proportions of silicon, and some cases manganese, chromium, nickel, tungsten, or other elements. Iron containing manganese combines with carbon more readily than other iron. Steel is grayish white, harder than cast iron or wrought iron, malleable, and ductile. It is very strong, withstanding great stress and strain. Steel melts at 1400° or above.

When very hot steel is suddenly cooled it becomes hard and brittle, but when it is cooled slowly it is soft and malleable. Hard steel becomes elastic when carefully heated and allowed to cool slowly. By suitably adjusting the conditions of heating and cooling, steel may be *tempered* to many desirable conditions of hardness or softness or elasticity.

Pieces of wrought iron or steel brought together on their clear surfaces and heated to a pasty condition may be *welded* into one piece by hammering or pressure. The electrical current is often used to heat iron and steel to the temperature required for welding.

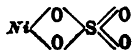
Nickel, Ni, 58.7

Nickel Minerals. Nickel is found native in small amounts in *meteorites*. The nickel of commerce is obtained from *garnierite*, $H_4Ni_2Mg_2(SiO_4)_3 \cdot 4\ H_2O$, a silicate found in Australia. It is also found in the minerals *niccolite*, NiAs, and *nickel glance* or *gersdorffite*, NiAsS. From *garnierite* crude nickel may be prepared by reducing the ore in the blast furnace or by electrolysis. The treatment of other nickel ores is a complicated process. Pure nickel may be obtained by heating nickel oxalate in a stream of hydrogen.

Nickel. *Nickel* is a white, lustrous metal of specific gravity 8.8 to 9.1, very hard and tenacious, and to some extent attracted by the magnet. It is not acted upon by air or water, and is attacked with difficulty by hydrochloric acid and by sulphuric acid, and readily by nitric acid, with formation of salts in which nickel is a bivalent positive ion.

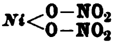
Nickel is usually marketed in the form of small cubes, which contain, besides nickel, small quantities of copper and bismuth and other metals. A number of *alloys* of nickel are important. *German silver* contains copper, zinc, and nickel. The United States five-cent piece contains 25 per cent. of nickel and 75 per cent. of copper. Nickel steel contains from 3 to 15 per cent. of nickel. Nickel is largely employed as a protective coating for iron, objects of iron to be *nickel-plated* being suitably connected in an electrical circuit while immersed in a bath or solution of nickel ammonium sulphate.

Nickel Salts. *Typical nickel compounds, in which nickel is a bivalent positive ion, are nickelous sulphate, nickelous nitrate, nickelous chloride, nickelous carbonate, nickelous sulphide, nickelous hydroxide, and nickelous oxide.*

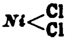


Nickelous sulphate, $NiSO_4$, is formed by acting upon nickel, or nickelous hydroxide or carbonate, with dilute

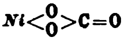
sulphuric acid. When crystallized from the water solution at 15 o
20°, it forms green crystals of the composition $NiSO_4 \cdot 7\,H_2O$. Th compound occurs native as the mineral ***morenosite*** (nickel vitri From a solution containing an excess of sulphuric acid, bluish gree crystals of the composition $NiSO_4 \cdot 6\,H_2O$ are obtained. When crystallized nickelous sulphate is heated to 100°, it is partially dehydrate forming $NiSO_4 \cdot H_2O$, which above 280° becomes anhydrous. By actin upon nickel with dilute sulphuric acid, and adding to the solution ammonium sulphate, crystals of $(NH_4)_2SO_4 \cdot NiSO_4 \cdot 6\,H_2O$ may be formed.


$Ni\begin{smallmatrix}<O-NO_2\\<O-NO_2\end{smallmatrix}$

Nickelous nitrate, $Ni(NO_3)_2$, may be obtained as crysta of the composition $Ni(NO_3)_2 \cdot 6\,H_2O$, by acting up nickel, or nickelous hydroxide, with nitric acid, and evaporating th solution.


$Ni\begin{smallmatrix}<Cl\\<Cl\end{smallmatrix}$

Nickelous chloride, $NiCl_2$, may be obtained by acting up finely divided nickel with chlorine, or by acting upon nickelous oxide or nickelous carbonate with hydrochloric acid. By evaporating the solution to dryness, the anhydrous nickelous chloride is obtain as a yellow earthy mass, which on exposure to moist air forms gre hydrous crystals, $NiCl_2 \cdot 6\,H_2O$. Nickelous chloride evolves chlor when heated in air.


$Ni\begin{smallmatrix}<O\\<O\end{smallmatrix}>C=O$

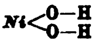
Nickelous carbonate, $NiCO_3$, is obtained as anhydr pale green crystals by heating a solution of nickelous ch ride with calcium carbonate at 150°. By evaporating at low temperat a solution of a nickel salt and sodium hydrogen carbonate saturat with carbon dioxide, crystals of the composition $NiCO_3 \cdot 6\,H_2O$ may b obtained. By adding sodium carbonate, or other soluble carbonate, to solution of nickelous sulphate or other nickel salt, a green precipitate a *basic nickelous carbonate* may be obtained, which is acted upon acid and by ammonium chloride and ammonium carbonate.

Ni=S

Nickelous sulphide, NiS, is formed as a black precipit when ammonium sulphide, $(NH_4)_2S$, or an alkali sulph is added to a solution of nickelous sulphate or other nickel salt.

$$NiSO_4 + (NH_4)_2S = \mathbf{NiS} + (NH_4)_2SO_4$$

The precipitate thus formed is not attacked by dilute hydrochl acid. Hydrogen sulphide will also precipitate nickelous sulphide fr solutions of nickel salts, but the reaction in this case is reversible a therefore not complete. Nickelous sulphide may be made as a bro yellow brittle mass by fusing together nickel and sulphur, and occurs as the mineral *millerite*. *Nickel disulphide*, NiS_2, is also known.



Nickelous hydroxide, $Ni(OH)_2$, is formed as an apple-green precipitate when sodium hydroxide, or any other soluble hydroxide, is added to a solution of a nickelous salt, such as nickelous sulphate.

$$NiSO_4 + 2\,NaOH = \mathbf{Ni(OH)_2} + Na_2SO_4$$

It is acted upon by ammonium hydroxides and by acids, and is decomposed by heating with formation of nickelous oxide.

Ni=O

Nickelous oxide, NiO (nickel monoxide), is formed as a green crystalline powder, by strongly heating to redness nickelous nitrate, or nickelous carbonate, or nickelous hydroxide.

$$Ni(OH)_2 = NiO + H_2O$$

It is reduced to nickel by hydrogen or carbon or carbon monoxide. It is acted upon by acids with formation of nickelous salts. Nickelous oxide occurs as the mineral *bunsenite*.

Nickelous fluoride, NiF_2, forms blue-green crystals of the composition $NiF_2 \cdot 3\,H_2O$. *Nickelous bromide*, $NiBr_2$, occurs as crystals of the composition $NiBr_2 \cdot 3\,H_2O$. *Nickelous iodide*, NiI_2, may be obtained as blue-green crystals of the composition $NiI_2 \cdot 6\,H_2O$.

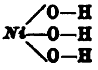
Potassium ferrocyanide, $K_4[Fe(CN)_6]$, precipitates from a solution of nickelous sulphate, $NiSO_4$, or other nickel salt, greenish white *nickelous ferrocyanide*, $Ni_2[Fe(CN)_6]$.

$$2\,NiSO_4 + K_4[Fe(CN)_6] = \mathbf{Ni_2[Fe(CN)_6]} + 2\,K_2SO_4$$

Potassium ferricyanide, $K_3[Fe(CN)_6]$, precipitates from solutions of nickel salts, yellowish green *nickelous ferricyanide*, $Ni_3[Fe(CN)_6]_2$.

$$3\,NiSO_4 + 2\,K_3[Fe(CN)_6] = \mathbf{Ni_3[Fe(CN)_6]_2} + 3\,K_2SO_4$$

Nickelic Compounds. *Nickelic hydroxide and nickelic oxide are compounds in which nickel is a trivalent positive ion.*



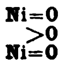
Nickelic hydroxide, $Ni(OH)_3$, may be obtained as a black powder by acting upon precipitated nickelous hydroxide with chlorine or bromine or a similar oxidizing agent.

$$3\,Ni(OH)_2 + Cl_2 = 2\,Ni(OH)_3 + NiCl_2$$

In presence of an alkali hydroxide all the nickel appears in nickelic hydroxide.

$$2\,Ni(OH)_2 + Cl_2 + 2\,NaOH = 2\,Ni(OH)_3 + 2\,NaCl$$

Nickelic hydroxide is acted upon by acids, with evolution of oxygen and formation of nickel salts.



$$\begin{matrix} Ni=O \\ \;\;>O \\ Ni=O \end{matrix}$$

Nickelic oxide, Ni_2O_3 (nickel sesquioxide), is obtained as a black powder by gently heating below redness nickelic hydroxide, nickel nitrate, or nickel carbonate, in air. When strongly heated it forms nickelous oxide.

$$2\,Ni_2O_3 = 4\,NiO + O_2$$

Nickelic oxide is acted upon by acids with formation of the nickel salts. By acting upon nickelic oxide with hydrochloric acid, nickelous chloride is formed, chlorine being liberated.

$$Ni_2O_8 + 6\,HCl = 2\,NiCl_2 + 3\,H_2O + Cl_2$$

By heating nickelic oxide in hydrogen at 190°, or by heating nickelous chloride in oxygen at 350° to 440°, *magnetic nickel oxide*, Ni_3O_4, is formed.

By the combination of nickel and carbon monoxide, CO, at ordinary temperature, a colorless, highly refractive liquid is formed which has the composition $Ni(CO)_4$, and is known as *nickel carbonyl*. It boils at 43° and forms crystals at −25°. When passed through a heated tube, it dissociates into carbon monoxide and nickel.

$$Ni + 4\,CO \rightleftarrows Ni(CO)_4$$

Summary. *Nickelous sulphate is formed by the action of dilute sulphuric acid upon nickel or nickelous hydroxide, or nickelous carbonate. Nickelous nitrate may be formed by acting with nitric acid upon nickel or nickelous hydroxide. Nickelous chloride may be obtained by acting upon nickel with chlorine, or by acting upon nickelous oxide or nickelous carbonate with hydrochloric acid. Nickelous carbonate may be made by heating nickelous chloride solution with calcium carbonate. Basic nickelous carbonates may be precipitated by adding a soluble carbonate to a solution of a nickel salt. Nickelous sulphide may be precipitated by adding ammonium sulphide, or an alkali sulphide, to a solution of a nickel salt. Nickel disulphide is also known.*

Nickelous hydroxide is precipitated when a soluble hydroxide is added to a nickel salt in solution. It is decomposed by heating, with formation *of nickelous oxide. Nickelous oxide is formed by heating nickelous nitrate, nickelous carbonate, or nickelous hydroxide.*

Other nickel compounds are nickelous fluoride, nickelous bromide, nickelous iodide, nickelous ferrocyanide, and nickelous ferricyanide.

Nickelic hydroxide may be formed by oxidizing nickelous hydroxide with chlorine or other suitable agents. Nickelic oxide is made by heating nickelic hydroxide below redness. When strongly heated, it forms nickelous oxide. It is acted upon by acids, with formation of nickelous salts. Magnetic nickel oxide is made by heating nickelic oxide in hydrogen, or by heating nickelous chloride in oxygen.

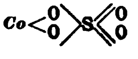
Nickel carbonyl is formed by the combination of nickel and carbon monoxide.

Cobalt, Co, 59.0

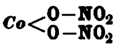
Cobalt Minerals. Cobalt is found associated with nickel in certain ores. The principal cobalt minerals are *smaltite*, $CoAs_2$ (cobalt glance), and *cobaltite*, CoAsS, from which cobalt is obtained by roasting and reducing the resulting oxide, Co_3O_4, by carbon or hydrogen. Cobalt compounds are used to impart a blue color to glass.

Cobalt. *Cobalt* is a lustrous pink metal, of specific gravity 8.5, malleable and ductile, and very tenacious. It melts at 1500°. In compact form cobalt is only very slightly tarnished by damp air, but the finely divided metal may oxidize easily, sometimes taking fire in the air spontaneously, burning to the oxide Co_3O_4. Cobalt is slowly attacked by warm dilute hydrochloric acid or sulphuric acid, and is rapidly acted on by nitric acid, with formation of salts in which cobalt is a bivalent or trivalent positive ion.

Cobaltous Compounds. *The principal compounds in which cobalt is a bivalent positive ion are cobaltous sulphate, cobaltous nitrate, cobaltous chloride, cobaltous carbonate, cobaltous sulphide, cobaltous hydroxide and cobaltous oxide.*

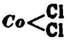


Cobaltous sulphate, $CoSO_4$, is obtained by acting upon cobalt, or the cobalt oxides, or upon cobaltous carbonate, with dilute sulphuric acid, and evaporating the solution. It forms red prismatic crystals of the composition $CoSO_4 \cdot 7\ H_2O$, which remain stable in air. When the solution is warmed and allowed to stand, crystals of the composition $CoSO_4 \cdot 6\ H_2O$ are formed. By the action of sulphuric acid upon a concentrated solution of cobaltous sulphate, a powder of the composition $CoSO_4 \cdot 4\ H_2O$ is formed. All these hydrates when heated lose their water, becoming rose-red in color.



$$Co<\begin{matrix}O-NO_2\\O-NO_2\end{matrix}$$

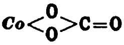
Cobaltous nitrate, $Co(NO_3)_2$, may be prepared by acting upon cobalt, or its oxides, hydroxides, or carbonates, with nitric acid. It forms deep red prismatic crystals, $Co(NO_3)_2 \cdot 6\ H_2O$, very hygroscopic, which melt below 100° to a violet liquid which upon strong heating turns green and decomposes. Cobalt nitrate is used as a reagent in blowpipe analysis for the production of cobalt compounds of characteristic color.



$$Co<\begin{matrix}Cl\\Cl\end{matrix}$$

Cobaltous chloride, $CoCl_2$, is obtained by acting upon cobalt, or its oxides, or hydroxides, or carbonates, with hydrochloric acid. It forms dark red prismatic crystals, having the composition $CoCl_2 \cdot 6\ H_2O$, which may be dehydrated in different stages, forming successively red or violet $CoCl_2 \cdot 4\ H_2O$ and $CoCl_2 \cdot 2\ H_2O$, and the blue anhydrous $CoCl_2$. The water solution of cobaltous chloride is rose-colored when concentrated, but becomes blue when heated or treated with concentrated hydrochloric acid.

When a solution of cobaltous chloride sufficiently dilute is used as an ink, the writing upon rose-colored paper is invisible when allowed to dry in the air at ordinary temperature, but when such writing is warmed, the characters appear bright blue, although they will fade away again gradually on standing in moist air. The use of cobaltous chloride as a sympathetic ink and in the toy weather-indicators depends on its property of changing color according to the conditions of moisture in the atmosphere.



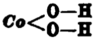
$$Co<\begin{matrix}O\\O\end{matrix}>C=O$$

Cobaltous carbonate, $CoCO_3$, is obtained as a bright red powder by heating a solution of cobaltous chloride and sodium hydrogen carbonate saturated with carbon dioxide. By spontaneous evaporation of the solution, crystals of the composition $CoCO_3 \cdot 6\ H_2O$ are formed. By the action of soluble carbonates upon cold solutions of cobaltous salts reddish *basic cobaltous carbonates* are formed, which on heating lose carbon dioxide and turn blue.

$Co=S$ *Cobaltous sulphide*, CoS (cobalt monosulphide), is obtained as a black precipitate when ammonium sulphide, $(NH_4)_2S$, or an alkali sulphide is added to a solution of cobalt chloride, $CoCl_2$, or other salt of cobalt.

$$CoCl_2 + (NH_4)_2S = \mathbf{CoS} + 2\ (NH_4)Cl$$

It is attacked by strong hydrochloric acid with evolution of hydrogen sulphide. Hydrogen sulphide precipitates cobaltous sulphide from salt solutions, but the reaction is only partial. Cobaltous sulphide is found as the mineral *syepoorite*. Other sulphides of cobalt are CoS_2, Co_2S_3, and Co_2S.


$Co<\begin{matrix}O-H\\O-H\end{matrix}$

Cobaltous hydroxide, $Co(OH)_2$, is a rose-red precipitate formed by adding a soluble hydroxide, such as sodium hydroxide, to a solution of cobaltous chloride or other cobaltous salt kept out of contact with air, and heating the resulting precipitate of blue basic salt.

$$CoCl_2 + 2\ NaOH = \mathbf{Co(OH)_2} + 2\ NaCl$$

Cobaltous hydroxide is acted upon by ammonium hydroxide and by acids. It combines with the oxygen upon standing in the air, becoming dark colored, and decomposes when heated.

$Co=O$

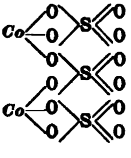
Cobaltous oxide, CoO (cobalt monoxide), is obtained by heating cobaltous hydroxide, or cobaltous carbonate, to a temperature not above 350°, in an atmosphere of hydrogen.

$$Co(OH)_2 = CoO + H_2O$$

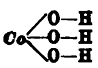
It may also be made by heating the higher oxides of cobalt to a white heat. It is acted upon by acids, with formation of cobaltous salts.

Cobaltous fluoride, CoF_2, *cobaltous bromide*, $CoBr_2$, and *cobaltous iodide*, CoI_2, are also known as brightly colored crystalline compounds. By the action of potassium ferrocyanide and potassium ferricyanide on cobaltous salts, the green *cobaltous ferrocyanide*, $Co_2[Fe(CN)_6]$, and the dark brown *cobaltous ferricyanide*, $Co_3[Fe(CN)_6]_2$, may be formed as precipitates.

Cobaltic Compounds. *Cobalt forms a few cobaltic compounds, — cobaltic sulphate, cobaltic hydroxide, and cobaltic oxide, — in which cobalt is a trivalent positive ion.*



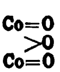
Cobaltic sulphate, $Co_2(SO_4)_3$, is formed as blue needles of the composition $Co_2(SO_4)_3 \cdot 18\ H_2O$, when a solution of cobaltous sulphate and sulphuric acid is oxidized by the electric current. It dissolves in water to form a blue solution which evolves oxygen. The crystals decompose on exposure to air, becoming pink. It is decomposed by hydrochloric acid, with evolution of chlorine.



Cobaltic hydroxide, $Co(OH)_3$, may be obtained by acting with sodium hydroxide and chlorine, bromine, sodium hypochlorite, or other suitable oxidizing agent upon a solution of a cobaltous salt.

$$2\,CoCl_2 + 6\,NaOH + Cl_2 = 2\,Co(OH)_3 + 6\,NaCl$$

It forms a brownish black powder, which is decomposed by hydrochloric acid with evolution of chlorine, and by sulphuric acid with evolution of oxygen, with formation of cobaltous salts. Several cobaltic oxyhydroxides, such as $Co_3O_2(OH)_4$, $Co_3O(OH)_6$, and $Co_3O_3(OH)_2$, have been isolated.



Cobaltic oxide, Co_2O_3 (cobalt sesquioxide), a dark brown powder, is made by heating cobaltous nitrate to a temperature just sufficient to decompose the salt. Cobaltic oxide is acted upon by hydrochloric acid with evolution of chlorine, and by sulphuric acid with evolution of oxygen, cobaltous chloride being formed.

Tricobalt tetroxide, Co_3O_4, corresponding to the magnetic oxides of iron and nickel, but itself non-magnetic, is formed when cobalt or its lower oxides or hydroxides are heated to low redness. It is a stable black powder.

Complex Cobalt Salts.

Cobalt enters into combination with the ions CN, NO_2, and NH_3 to form complex derivatives.

Cobalt and cyanogen together constitute a negative ion in certain compounds known as the *cobaltocyanides* and *cobalticyanides*. Thus the insoluble *cobaltous cyanide*, $Co(CN)_2$, combines with potassium cyanide, KCN, to form soluble *potassium cobaltocyanide*, $K_4Co(CN)_6$, which oxidizes in the air to form soluble *potassium cobalticyanide*, $K_3Co(CN)_6$. When potassium nitrite is added to the solution of a cobaltous salt, a double nitrite of potassium and cobalt, $2\,KNO_2 \cdot Co(NO_2)_2$, is formed in the solution, from which on the addition of considerable acetic acid there is formed and precipitated after some time yellow crystalline *potassium cobaltinitrite*, $K_3Co(NO_2)_6$, which is probably best regarded as a salt of potassium in which that element is combined with a complex nitroso-cobaltic ion.

Cobalt Amines.

The compounds of ammonia with cobalt present many interesting but very complex relations. When a solution of cobaltous chloride is treated with ammonium hydroxide, cobaltous hydroxide is at first precipitated, but is acted upon when the ammonium hydroxide is added in sufficient amount. The brown solution thus formed takes up oxygen and turns red on standing in the air, and from it by the action of hydrochloric acid, after more or less oxidation either by exposure to air or by the aid of oxidizing agents, a series of salts known as the *cobalt amines* may be obtained.

Of these compounds we may mention the following:

Dichro-cobaltic chloride, $Co(NH_3)_3Cl_3 \cdot H_2O$
Praseo-cobaltic chloride, $Co(NH_3)_4Cl_3 \cdot H_2O$
Purpureo-cobaltic chloride, $Co(NH_3)_5Cl_3$
Luteo-cobaltic chloride, $Co(NH_3)_6Cl_3$

These salts consist of cobalt and chlorine in proportions to form cobaltic chloride with varying numbers of equivalents of ammonia. Cobalt amine nitrates and sulphates similar to the chlorides mentioned may also be obtained.

When luteo-cobaltic chloride, $Co(NH_3)_6Cl_3$, is treated in solution with silver nitrate, silver chloride is precipitated, and the precipitate contains the entire amount of chlorine originally present in the cobaltic chloride, the ions of this substance being, therefore, $Co(NH_3)_6$, and Cl_3. By loss of one equivalent of ammonia, luteo-cobaltic chloride is converted to purpureo-cobaltic chloride, $Co(NH_3)_5Cl_3$, and this when treated with silver nitrate loses only two thirds of its chlorine by the formation of silver chloride; so that the ions in this case are $Co(NH_3)_5Cl$ and Cl_2. Similarly, praseo-cobaltic chloride, $Co(NH_3)_4Cl_3 \cdot H_2O$, yielding but one third of its chlorine when acted upon by silver nitrate, may be represented by the symbol $Co(NH_3)_4Cl_2 \cdot Cl \cdot H_2O$.

Werner has proposed to regard the molecules of these compounds as made up of a nucleus of one cobalt atom with six atoms or radicals, CoR_6, to which other ions may be joined, any ion external to the nucleus being displaceable without disturbing the nucleus. Moreover, the characters of the elements or radicals composing the nucleus determine the capacity of the nucleus to unite with ions, and also the kind of ions, positive or negative, with which it may unite. The conception of the nucleus as an octahedron, at the center of which is the cobalt atom and near which are arranged the external ions, serves to give graphic representation of the phenomena.

In the case of the cobalt amines we start with luteo-cobaltic chloride in which the nucleus is $Co(NH_3)_6$, and the outlying ions, 3 Cl, are negative and three in number. Purpureo-cobaltic chloride consists of a nucleus $Co(NH_3)_5Cl$, with two outlying negative ions, 2 Cl. Praseo-cobaltic chloride is made up of the nucleus $Co(NH_3)_4Cl_2$, with one outlying negative ion, Cl. The substance $Co(NH_3)_3Cl_3$ is all nucleus, and the further introduction of negative atoms or radicals within the nucleus should make it negative. It is interesting to note that we have in potassium cobalticyanide, which may be written $Co(CN)_6 \cdot K_3$, and in the potassium cobaltinitrite, which may be written $Co(NO_3)_6 \cdot K_3$, examples of cobaltic compounds each of which may be regarded as made up of a negative nucleus, CoR_6, united with three outlying positive ions 3 K. Potassium cobaltocyanide, $K_4Co(CN)_6$, may in like manner be written $Co(CN)_6 \cdot K_4$.

Summary. *Cobaltous sulphate is made by acting with dilute sulphuric acid upon cobalt, cobalt oxides, or cobaltous carbonate. Cobaltous nitrate may be made by acting with nitric acid upon cobalt, or its oxides, hydroxides, or carbonate. Cobaltous chloride may be made by acting with hydrochloric acid upon cobalt, or its oxides or hydroxides or carbonate. Cobaltous carbonate may be made by heating a solution of cobaltous chloride and sodium hydrogen carbonate which has been saturated with carbon dioxide. Cobaltous sulphide may be precipitated by adding ammonium sulphide or an alkali sulphide to a cobalt salt in solution.*

Cobaltous hydroxide may be precipitated by adding a soluble hydroxide to a solution containing a cobalt salt. It is attacked by acids with formation of cobaltous salts. Cobaltous oxide is made by heating cobaltous hydroxide or cobaltous carbonate to a temperature not too high, in an atmosphere of hydrogen.

Other cobaltous compounds are cobaltous fluoride, cobaltous bromide, cobaltous iodide, cobaltous ferrocyanide, and cobaltous ferricyanide.

Cobaltic sulphate is made by oxidizing cobaltous sulphate by the electric current.

Cobaltic hydroxide may be made by the action of a soluble hydroxide and an oxidizing agent upon a solution of a cobaltous salt.

Cobaltic oxide is made by heating cobaltous nitrate to a suitable temperature. Tricobalt tetroxide may be made by heating cobalt or its lower oxides or hydroxide to low redness.

Complex compounds of cobalt, such as cobaltous cyanide, the cobaltocyanides and cobalticyanides, the double salts known as cobaltinitrites, and the ammonia derivatives known as cobalt amines may also be prepared.

II. THE PLATINUM ELEMENTS

a. Ruthenium, Ru, 101.7
Rhodium, Rh, 103.0
Palladium, Pd, 106.5

b. Osmium, Os, 191
Iridium, Ir, 193.0
Platinum, Pt, 194.8

The rare elements of the eighth group of the secondary series, including the useful element platinum, and the five other elements of similar properties, ruthenium, rhodium, palladium, osmium, and iridium, together constitute the group of *platinum elements.*

Native platinum ore, containing all these six elements in varying amounts, with usually some gold and perhaps other elements, is found generally in small metallic grains in sand, and is obtained by washing away the lighter materials of the sand, as in gold washing. The largest amounts of platinum come from the Ural Mountains; but California, Australia, Sumatra, and some other regions contribute in smaller degree to the supply. From the crude ore a useful alloy of platinum with iridium and rhodium may be obtained directly by fusion of the ore on lime in the oxyhydrogen flame, but the complete separation of the platinum metals from one another involves elaborate processes of treatment.

The platinum metals fall into two series, the one consisting of the metals ruthenium, rhodium, and palladium, of atomic weights approximating 100, while the other contains the metals osmium, iridium, and platinum, of atomic weight nearly twice as great. The compounds of each of these series of metals show many resemblances to one another, and to the series of the iron metals.

Ruthenium, a metal of steel-gray color and specific gravity 12.26, hard, brittle, and fusible above 2000°, was discovered by Claus in 1845. Heated in finely divided condition in air, the metal oxidizes with the formation of three oxides: *ruthenium monoxide,* RuO, *ruthenium sesquioxide,* Ru_2O_3, and *ruthenium dioxide,* RuO_2, all black powders, unacted upon by acids; while *ruthenium tetroxide,* RuO_4, yellow, crystalline, boiling at 26°, may be obtained by indirect means, as will be described. The dark brown weakly basic *ruthenium hydroxide,* $Ru(OH)_3$, corresponding to the sesquioxide, and the dark brown gelatinous hydroxide, $Ru(OH)_4 \cdot 3\,H_2O$, acted upon by both acids and alkali hydroxides, and corresponding to the oxide, RuO, are also known. Heated in chlorine, ruthenium forms *ruthenium dichloride,* $RuCl_2$, a black powder, unaffected by acids. Although ruthenium is not attacked by single acids, it is slowly acted upon by aqua regia, forming in solution *ruthenium trichloride,* $RuCl_3$, which may be obtained as a yellow crystalline deliquescent solid. *Ruthenium tetrachloride*, $RuCl_4$, has not been isolated, but exists in certain double salts.

When fused with potassium hydroxide and potassium nitrate in mixture, finely divided ruthenium is attacked with formation of *potassium ruthenate*, K_2RuO_4, which may be obtained in black crystals of green reflection. The dark orange-red solution of potassium ruthenate in water is turned green by air, and more rapidly by chlorine or bromine, while ruthenium dioxide, RuO_2, separates, and *potassium perruthenate*, $KRuO_4$, crystallizable in black octahedra, is formed. The action of chlorine upon a concentrated solution of potassium ruthenate, K_2RuO_4, results in the formation of *ruthenium tetroxide*, RuO_4, which volatilizes with the chlorine and may be condensed by cooling, and is useful in the preparation of pure ruthenium.

Rhodium, discovered by Wollaston in 1803, in appearance like aluminium, of specific gravity 12.1, very malleable, fusing at 2000°, is not attacked by single acids nor when pure by aqua regia. Heated in air, it is oxidized to *rhodium monoxide*, RhO ; fused with a mixture of potassium nitrate and potassium hydroxide it is attacked, the resulting mass when treated with acid leaving gray, metallic *rhodium sesquioxide*, Rh_2O_3, or gray metallic *rhodium dioxide*, RhO_2, according to the conditions of treatment, or a mixture of both these oxides. The *rhodium hydroxide*, $Rh(OH)_3$, black, weakly acidic, and basic, and the green, powdery *rhodium hydroxide*, $Rh(OH)_4$, corresponding respectively to the oxide Rh_2O_3, and the oxide RhO_2, are known. When heated in chlorine gas, the metal yields brownish red *rhodium trichloride*, $RhCl_3$, which is capable of entering into combination with alkali chlorides to form double salts. From *chlorpurpureo-rhodium chloride*, $Rh(NH_3)_5Cl_3$, one of many existing complex ammonia compounds, rhodium may be prepared in pure condition.

Palladium, a silvery white metal of specific gravity 11.9 and melting at 1500°, was discovered by Wollaston in 1803. When finely divided, palladium is attacked by boiling and concentrated hydrochloric acid, by nitric acid, and by sulphuric acid. The most striking peculiarity of palladium is its capacity to occlude hydrogen to the extent of 370 times its own volume when in thin foil at ordinary temperatures, 650 times its own volume at 90° to 100°, 800 times its own volume when finely divided, and as much as 960 times its own volume when made the negative pole in an electrolytic cell in which water is undergoing electrolysis. The *palladium-hydrogen* thus formed, though of greater specific volume and lower specific gravity than palladium, has the appearance of palladium. It loses hydrogen at 130° under atmospheric pressure, and yields all its hydrogen when heated in a vacuum. The nature of the union of the elements in the palladium-hydrogen is not fully understood. The earlier view that a definite *palladium hydride*, Pd_2H, is formed appears to be untenable in the light of recent investigation, but the newer idea that the material is simply a "solid solution" in which gaseous hydrogen is dissolved in solid palladium meets with some difficulty in the fact that the dissociation of palladium-hydrogen does not proceed with regularity independent of the composition of this substance. Palladium-hydrogen is a powerful reducer, releasing hydrogen in active form as if "nascent," and capable of reducing ferric salts to the ferrous condition and of acting upon chlorine to form hydrochloric acid and upon iodine to form hydriodic acid.

Palladium acts as a positive ion in series of palladium salts, in which it shows a valence of II. *Palladious nitrate*, $Pd(NO_3)_2$, dark brown and deliquescent, is formed when palladium and nitric acid react; brown deliquescent *palladious chloride*, $PdCl_2$, is left when the solution formed by acting upon palladium with aqua regia is evaporated to dryness, and compounds of palladious chloride with alkali chlorides, such as K_2PdCl_4, in which the bivalent palladium is the constituent of the negative ion, are easily formed; black *palladious iodide*, PdI_2, is precipitated from palladium salts by potassium iodide; crystallized brown *palladious sulphate*, $PdSO_4 \cdot 2\ H_2O$, is obtained by the action of sulphuric acid upon palladium. Black *palladious oxide*, PdO, left upon careful ignition of palladium nitrate, when heated to redness loses half its oxygen, with formation of *palladium suboxide*, Pd_2O, and at white heat forms the metal; black *palladium dioxide*, PdO_2, and a corresponding hydroxide, weakly acidic and basic, are formed by the action of an alkali hydroxide upon palladious tetrachloride. *Palladium tetrachloride*, $PdCl_4$, in which quadrivalent chlorine is the positive ion, and *chlorpalladic acid*, H_2PdCl_6, in which quadrivalent palladium is a constituent of the negative ion, are produced in solution when palladium is acted upon by aqua regia. Upon this solution ammonium chloride and alkali chlorides act to form chlorpalladates, such as red *potassium chlorpalladate*, K_2PdCl_6, and red *ammonium chlorpalladate*, $(NH_4)_2PdCl_6$, difficulty soluble in water.

Osmium, discovered by Tennant in 1804, the heaviest of the metals, of specific gravity of 22.4, fusing only at 2500°, is obtained as a black powder, or as crystals with metallic luster. Ignited in fine powder, the metal burns in air, forming white *osmium tetroxide*, OsO_4, fusible below 100°, capable of distilling at somewhat higher temperature, slowly soluble in water to a solution of neutral reaction, volatile in steam, of unpleasant odor, suggesting sulphur chloride, irritating to the eyes and mucous membrane, easily reduced to metal, and useful in hardening tissues for microscopic examination. Other oxides, *osmium dioxide*, OsO_2, *osmium sesquioxide*, Os_2O_3, and *osmium monoxide*, OsO, have been prepared by fusing suitable salts of osmium with sodium carbonate. A blue-black *osmium hydroxide*, $Os(OH)_2$, very sensitive to the action of the air, may possibly exist; brown-red *osmium trihydroxide*, $Os(OH)_3$, appears to be both weakly basic and weakly acidic; the oxyhydroxide, $OsO(OH)_2$, corresponding to osmium dioxide, OsO_2, has acidic properties; while no hydroxide and no salts corresponding to osmium tetroxide are known.

By fusing osmium compounds with potassium hydroxide and potassium nitrate, *potassium osmiate*, K_2OsO_4, is formed, which dissolves in wat and crystallizes in the form of dark violet octahedra, $K_2OsO_4 \cdot 2\ H_2O$. Neither the acid nor the oxide corresponding to this salt is known. Three chlorides of osmium are formed by the action of chlorine on the metal: dark green *osmium dichloride*, $OsCl_2$; purple *osmium trichloride*, $OsCl_3$, and red *osmium tetrachloride*, $OsCl_4$. ***Iridosmine***, an alloy of osmium with iridium, the residue of the extraction of platinum ore by aqua regia, is hard, and finds application in tipping gold pens.

Iridium, a silvery metal of specific gravity 22.38, hard, fusible at 1950° in the oxyhydrogen flame, was discovered by Tennant in 1804. It may be separated from iridosmine by forming and volatilizing osmium tetroxide in a current of oxygen. It alloys with platinum, and enhances the useful properties of that metal for laboratory purposes, and is generally present in platinum utensils. Pure iridium, even when finely divided, is slowly attacked by aqua regia. Iridium forms three chlorides: dark olive-green, *iridium dichloride*, $IrCl_2$, and bright olive-green, *iridium trichloride*, $IrCl_3$, formed by ignition of the finely divided metal in chlorine, and *iridium tetrachloride*, $IrCl_4$, formed by the action of aqua regia upon the metal. Iridium trichloride forms with alkali chlorides double salts, such as $K_3IrCl_6 \cdot 3\ H_2O$; and iridium tetrachloride dissolves in water to form *chloriridic acid*, H_2IrCl_6, which acts upon alkali chlorides to form *chloriridates*, such as K_2IrCl_6 and $(NH_4)_2IrCl_6$. From the iridium chlorides may be obtained the three oxides: black *iridium monoxide*, IrO, blue-black *iridium sesquioxide*, IrO, and black *iridium dioxide*, IrO_2. A black *iridium trihydroxide*, $Ir(OH)_3$, of weak basic properties, corresponding to the sesquioxide, Ir_2O_3, and an indigo-blue *iridium tetrahydroxide*, $Ir(OH)_4$, of neutral behavior, corresponding to iridium dioxide, IrO_2, are known.

Platinum is a grayish white metal of specific gravity 21.45, tough, malleable, ductile, softening at red heat and capable of welding, fusing at 1770° in the oxyhydrogen flame. It occludes hydrogen and oxygen more or less according to its state of division, the finely divided "platinum black," obtained by precipitating the metal from its salts by a more electro-positive metal, like zinc, being capable of absorbing as much as 310 times its own volume of hydrogen and 100 times its own volume of oxygen, each of these gases being fully expelled from the metal at red heat. To this capacity of platinum to occlude oxygen and hydrogen is due the value of platinum as a "catalytic agent" in many processes. The "contact process" for making sulphur trioxide by passing sulphur dioxide with oxygen over spongy platinum, obtained by igniting *ammonium chlorplatinate*, $(NH_4)_2PtCl_6$, as well as the automatic gas-lighters, which ignite illuminating gas projected against a bit of spongy platinum previously exposed to air, work by reason of this property of platinum.

When platinum is disintegrated by passing an electric arc between platinum poles immersed in water, the finely divided platinum forms a colloidal solution and exhibits catalytic effects. Platinum resists this action of many common laboratory reagents, and for this reason is especially useful as material for laboratory utensils. It is not attacked by most acids or bases in solution, or even by the alkali carbonates in a state of fusion. It is, however, acted upon by alkali hydroxides, sulphides, and cyanides, at red heat; and it forms alloys with many metals, as well as with phosphorus, arsenic, and other less common elements.

Platinum shows a valence of II or IV, and forms compounds in which it is a constituent of the negative ion as well as compounds in which it is the positive ion.

When platinum is acted upon by aqua regia, the solution containing an excess of hydrochloric acid leaves upon evaporation reddish brown hygroscopic crystals of *chlorplatinic acid*, $H_2PtCl_6 \cdot 6\,H_2O$. From the suitably concentrated solution of this compound, potassium chloride precipitates difficultly soluble *potassium chlorplatinate*, K_2PtCl_6,

$$H_4PtCl_6 + 2\,KCl = K_2PtCl_6 + 2\,HCl$$

and ammonium chloride behaves similarly, forming the difficultly soluble *ammonium chlorplatinate*, $(NH_4)_2PtCl_6$. The *chlorplatinates* of rubidium, cæsium, and thallium are likewise difficultly soluble, but *sodium chlorplatinate*, Na_2PtCl_6, is very soluble in water and in alcohol. Upon this difference in the properties of the *chlorplatinates* rests the best method available for the analytical separation and determination of sodium and potassium in the salts. Upon ignition the chlorplatinates are decomposed, the alkali chlorplatinates leaving spongy platinum and the corresponding alkali chlorides, while ammonium chlorplatinate leaves pure spongy platinum, the ammonium chloride volatilizing.

Carefully heated in an atmosphere of chlorine, chlorplatinic acid, H_2PtCl_6, liberates hydrochloric acid, and reddish brown crystalline non-hygroscopic *platinum tetrachloride*, $PtCl_4$, remains. Upon treating a solution of chlorplatinic acid or of platinum tetrachloride with sodium hydroxide, and then with acetic acid, a reddish brown precipitate of *platinic hydroxide*, $Pt(OH)_4$, is formed. This hydroxide is acted upon by each of several acids, though not by acetic acid, and by alkali hydroxides, and so may be either basic or acidic according to conditions. By heating chlorplatinic acid to 200°, green, insoluble *platinum dichloride*, $PtCl_2$, is formed, which with alkali chlorides yields *chlorplatinites*, such as Na_2PtCl_4, *sodium chlorplatinite*, which upon ignition yields chlorine and platinum. When digested with an alkali hydroxide, platinum dichloride yields black *platinous hydroxide*, $Pt(OH)_2$, both basic and acidic.

Sulphides of platinum, PtS and PtS_2, are known, corresponding to the oxides. Certain double cyanides or salts of the hypothetical *cyanplatinous acid* are recognized, one of which, *barium cyanplatinite* or *barium platinocyanide*, $BaPt(CN)_4 \cdot 4\,H_2O$, is useful in making visible the Röntgen rays. Two series of platinum ammonium compounds, derived by the action of ammonia upon platinum dichloride and platinum tetrachloride, show interesting relations of an intricate nature.

CHAPTER XIX

TERTIARY SERIES — GROUPS I-VIII

GROUP I. SAMARIUM, Sm, 150
THULIUM, Tm, 171
GROUP II. YTTERBIUM, Yb, 173.0
GROUP III. GADOLINIUM, Gd, 156
GROUP IV. TERBIUM, Tb, 160
GROUP V. PRASEODYMIUM, Pr, 140.5
GROUP VI. NEODYMIUM, Nd, 143.6
ERBIUM, Er, 166
GROUP VII. ——
GROUP VIII. ——

THE relationship between the elements of the different groups of the Tertiary Series is so very close that the entire series might well be regarded as a single group of allied divisions after the analogy of the divisions *a*, *b*, *c*, of Group VIII, in the Secondary Series.

The elements ***samarium***, ***thulium***, ***ytterbium***, ***gadolinium***, ***terbium***, ***praseodymium***, ***neodymium***, and ***erbium***, have none of them been isolated in pure elementary form, but many of their salts have been prepared. These elements occur in certain rare minerals, and in their compounds they generally play the part of trivalent elements like aluminium. The oxides and hydroxides of the elements are insoluble in water, the chlorides and nitrates are soluble, the sulphates are soluble, but some of them form with potassium sulphate double salts difficultly soluble in the presence of an excess of potassium sulphate. The fact that the nitrates of these elements are decomposed by heat at varying temperatures makes it possible to use a fractional decomposition of the nitrates for the purpose of effecting separations of the compounds of the elements. The salts of many of these elements show characteristic absorption spectra, and the oxides when heated in the Bunsen flame become highly luminous. The study of the elements of this group, surrounded as it is with much difficulty, has been characterized by the announcement of the discovery of new elements, whose existence has afterwards been doubted, and in some cases disproved. At the present time the question of the existence of the elements ***carolinium*** and ***berzelium***, recently announced by Baskerville, is a matter of interest.

The history of the isolation of the compounds of the elements praseodymium and neodymium is typical. In 1839 Mosander prepared from the mineral *cerite* certain salts, among others, which he regarded as compounds of the single element *didymium*. For more than fifty years the elementary character of didymium was accepted, until Auer von Welsbach, by a most laborious process of fractional precipitation of the double nitrate of didymium and ammonium, succeeded in isolating two distinctly different double nitrates, $2\ NH_4NO_3 \cdot Pr(NO_3)_3 \cdot 4\ H_2O$ and $2\ NH_4(NO_3) \cdot Nd(NO_3)_3 \cdot 4\ H_2O$, from which were prepared two different series of salts, of different elements, which were now named *praseodymium* and *neodymium*. The praseodymium salts are leek-green, while the neodymium salts are rose-violet; and the absorption spectra of solutions of the salts are correspondingly characteristic.

Associated with the element yttrium in the mineral *gadolinite* occur in combination the other known elements of the tertiary series, *samarium*, *thulium*, *ytterbium*, *gadolinium*, *terbium*, and *erbium*, none of which, however, has been prepared in free condition.

In the accompanying table are given the symbols of some characteristic compounds of the elements of the tertiary series:

Samarium, Sm_2O_3, $Sm_2O_3 \cdot 6\ H_2O$, $SmCl_3 \cdot 6\ H_2O$, $Sm_2(SO_4)_3 \cdot 8\ H_2O$, $Sm(NO_3)_2 \cdot 6\ H_2O$, $Sm_2(CO_3)_2 \cdot 3\ H_2O$.

Thulium, Tm_2O_3(?), $Tm_2(SO_4)_3$, (?), $Tm(NO_3)_3$(?).

Ytterbium, Yb_2O_3, $Yb_2O_3 \cdot 6\ H_2O$, $Yb_2(SO_4)_3 \cdot 8\ H_2O$.

Gadolinium, Gd_2O_3, $Gd(SO_4)_3 \cdot 8\ H_2O$, $GdCl_3 \cdot 6\ H_2O$, $Gd(NO_3)_3 \cdot 6\ H_2O$, $Gd_2(CO_3)_3 \cdot 13\ H_2O$.

Terbium, Tb_2O_3, $Tb_2O_3 \cdot 6\ H_2O$, $Tb_2(SO_4)_3 \cdot 8\ H_2O$, $Tb(NO_3)_3 \cdot 6\ H_2O$, $Tb_2(CO_3)_3 \cdot nH_2O$.

Praseodymium, Pr_2O_3, Pr_4O_7, Pr_2O_4, Pr_2O_5, $PrCl_3 \cdot 7\ H_2O$, $Pr_2(SO_4)_3 \cdot 8\ H_2O$, $Pr_2O_2SO_4$, $PrH_3(SO_4)_3$, $Pr(NO_3)_3 \cdot 6\ H_2O$, $Pr_2(CO_3)_3 \cdot 8\ H_2O$, Pr_2S_3.

Neodymium, Nd_2O_3, Nd_2O_4(?), Nd_2O_5, $NdCl_3 \cdot 6\ H_2O$, $Nd_2(SO_4)_3 \cdot 8\ H_2O$, $Nd_2O_2SO_4$, $NdH_3(SO_4)_3$, $Nd(NO_3)_3$, Nd_2S_3.

Erbium, Er_2O_3, Er_2O_5, $Er_2O(OH)_4$, $ErCl_3$, $Er_2(SO_4)_3 \cdot 8\ H_2O$, $Er(NO_3)_3 \cdot 6\ H_2O$, $Er_2O_3(CO_2)_2 \cdot 2\ H_2O$, Er_2S_3.

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